ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON OXIDES OF TIN AND NICKEL

BY

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Dedicated to my parents, brothers and sisters

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Thanks to Almighty Allah who gave me the courage to accomplish this work successfully.

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LIST OF SYMBOLS

Ag/AgCl	Silver / Silver Chloride
CA	Chronoamperometry
ECR	Electrochemical Reduction of Carbon dioxide
EDX	Energy Dispersive X-ray Spectroscopy
FE	Faradaic Efficiency
GC	Gas Chromatography
IPCC	Intergovernmental Panel on Climate Change
LSV	Linear Sweep Voltammetry
MEA	Membrane Electrode Assembly
MWCNT	Multi Walled Carbon Nano Tubes
NHE	Normal Hydrogen Electrode
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
TCD	Thermal Conductivity Detector
XRD	X-ray Diffraction

ABSTRACT

NAME	**SHAHID MUHAMMAD BASHIR**
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In this MS Thesis, electrochemical reduction of carbon dioxide has been studied on high surface area multi walled carbon nano tubes (MWCNT) supported nickel oxide and tin oxide catalysts. Both the nickel and tin oxides catalysts were synthesized by direct impregnation method with different loading of metal content to get 10 %, 20 %, 30 % and 40 % metal oxide loaded on the support. The prepared catalysts were characterized using XRD and SEM-EDX determining the crystalline size, surface morphology, dispersion and metal oxide content on the support. Both XRD and SEM analysis shows that increase in the metal oxide content results in the poor dispersion due to agglomeration of the metal crystals. Electrochemical evaluation of the catalysts was carried out in a half cell (H-cell) and in an electrochemical reactor for carbon dioxide reduction. Linear sweep voltammetry (LSV) and chronoamperometry (CA) techniques were employed to study the electrochemical behavior of the catalysts. Half cell reaction setup was used to identify the optimum loading of the catalyst among the prepared sample. Based on LSV and CA for the carbon dioxide reduction process it was found that with the 20 % NiO/MWCNT and 20 % SnO_2/MWCNT catalysts optimum reaction rate. The selected catalyst, 20 % NiO/ MWCNT was further evaluated in the electrochemical reactor. The products obtained were mainly CO and H_2. The maximum faradaic efficiency obtained with 20 % NiO /MWCNT was at a potential of -1.7 V vs. NHE.

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ملخص الرسالة

الإســــــــــــم: شاهد محمد بشير

عنوان الرسالة: الاختزال الكهروكيميائي لثاني اكسيد الكربون على اكاسيد القصدير والنيكل

التخصـــــص: هندســـة كيميـــــائية

تأريخ الدرجة : أبريل 2012

في هذه الأطروحة ، تم دراسة الاختزال الكهروكيميائي لثاني اكسيد الكربون على حفازات اكاسيد القصدير والنيكل المدعمة على انابيب الكربون المتناهية الصغر ذات المساحة السطحية العالية. تم تحضير حفازات اكاسيد القصدير والنيكل باستخدام طريقة التطعيم المباشر بتراكيز معدنية مختلفة للحصول على أكاسيد معدنية على دعامة بتراكيز 10% و20% و 30% و40% . تم توصيف الحفازات المحضرة باستخدام اجهزة XRD و SEM-EDX لايجاد الحجم البلوري والسطح المورفولوجي والانتشار ومحتوى اكسيد المعدن على الدعامة. أظهرت نتائج تحليل كل من XRD و SEM ان الزيادة في تركيز محتوى اكسيد المعدن يؤدي الى انخفاض الانتشاربسبب تكتل بلورات المعدن.التقييم الكهروكيميائي لحفازات اختزال ثاني اكسيد الكربون تم باستخدام H-cell والمفاعل الكهروكيميائي.تم في هذا البحث أيضا استخدام تقنيات LSV و CA لدراسة السلوك الكهروكيميائي للحفازات وتم أيضا استخدام تفاعل نصف الخلية لاجل ايجاد التركيزالامثل للحفاز. بناءا على نتائج LSV و CA لعملية اختزال ثاني اكسيد الكربون, وجد ان التركيز 20% لكل من NiO/MWCNT و SnO2/MWCNT أعطى أعلى معدل للتفاعل.تم اختيار حفاز 20% NiO/MWCNT للتقييم في المفاعل الكهروكيميائي وتم الحصول على اول أكسيد الكربون والهيدروجين كنواتج للتفاعل.أقصى كفاءة للتيار كانت باستخدام حفاز 20% NiO/MWCNT عند جهد 1.7 V- بواسطة NHE .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران, المملكة العربية السعودية

Chapter 1

INTRODUCTION

1.1 Role of Carbon Dioxide

Carbon dioxide is the fourth abundant gas in the earth atmosphere. It is naturally available in our atmosphere but in the last few decades there is a gradual increase in the concentration of the atmospheric carbon dioxide. The primary reason for the rapid growth of carbon dioxide gas results from the combustion of the fossils fuels for power generation, transportation and emissions from the industries. Due to high population growth rate and dependency of the human race on the fossil fuel, the release of carbon dioxide is becoming more prominent.

Among different carbon dioxide sources, fossil fuel based power plants produced the largest amount of carbon dioxide up 32 %, followed by the emissions from the petroleum and petrochemical industries where burning of fossil fuel in the furnace releases carbon dioxide. Figure 1.1 shows the rate of increase of the carbon dioxide from 1960 to 2010 (Scripps 2011; Jiang et al. 2010; Song 2002; Scibioh et al. 2004).

Carbon dioxide is considered as a major contributor to the greenhouse effect. The greenhouse effect is the absorption of infrared radiation by the atmospheric gases resulting in the trapping of heat, which results in heating of Earth's surface (IPCC 2007). As a result, the temperature of the earth is increasing with increasing the greenhouse gas

in the atmosphere. Studies suggests that the rise in temperature will have long term effects as the glaciers in the colder regions like Arctic and Antarctic starts to melt leads to increase in the sea level which may cause water floods in the future. Furthermore, due to deforestation and continuous absorption in the oceans, the pH of the water increases which is harmful for marine life (IPCC 2007). So overall carbon dioxide is playing a negative role in our planet and due to its negative role the global communities are now more concern about the mitigation of this greenhouse gas.

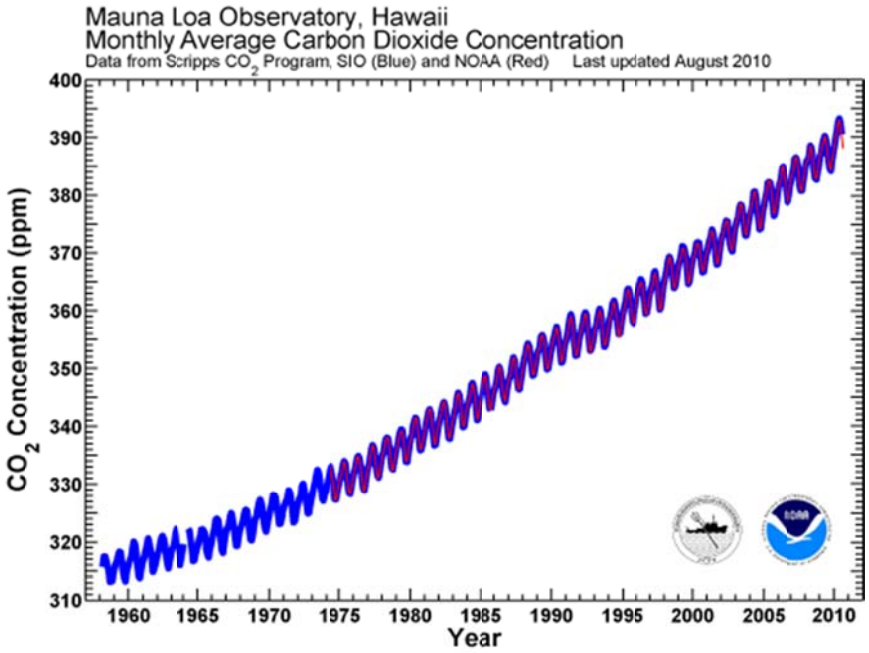

Figure 1.1: Concentration of CO_2 in the atmosphere (Scripps 2011)

1.2 Carbon Dioxide Control and Utilization

At present there are different steps being investigated to mitigate the concentration of carbon dioxide into the atmosphere. Especially, several alternative technologies have been under development stage to reduce the amount of carbon dioxide from the atmosphere. These include the carbon dioxide capture and sequestration, energy sources (green energy source or alternative energy source) free of carbon emissions and carbon dioxide conversion to different products (Song 2002).

1.2.1 Carbon Dioxide Capture and Sequestration

The first steps of CO_2 minimization is the separation and capture of CO_2 from the fossil fuel combustion sources. In this regard, it is possibly more effective of targeting the large sources of CO_2 such as fossil fuel based power generating plants. Conventionally, the technology used for CO_2 capture includes the absorption of CO_2 using strong CO_2 absorbing agents such as amines but the cost of using such process is very high. Given the facts, there are several alternative CO_2 capture technologies currently under development stage. Among them, chemical-looping combustion (CLC) is possibly the most promising low cost CO_2 capture technology (Hossain and de Lasa, 2008).

The captured CO_2 must be sequestrated safe in locations and/or converted into useful products. One of the most useful applications of CO_2 is the enhanced oil recovery. The injection of CO_2 into the pressure depleted oil reservoir increases the production of the oil from the reservoirs up to 10-15 %. Figure 1.2 shows the recovery of oil by CO_2 injection (Cano 2011; Davison et al. 2001).

Sequestration techniques include terrestrial sequestration and ocean sequestration. In terrestrial sequestration efforts have been made to develop processes to increase the level of carbon in the soil, biomass and wood products. Ocean sequestration involves the storing or consuming of carbon dioxide into the oceans by biological uptakes, passive air sea exchange and ocean mixing but the dumping of CO_2 with the ocean ultimately increases the pH of the water and creates harm for the life of the ocean creatures. (U.S. Climate Change Technology Program 2006; Sabine et al. 2004).

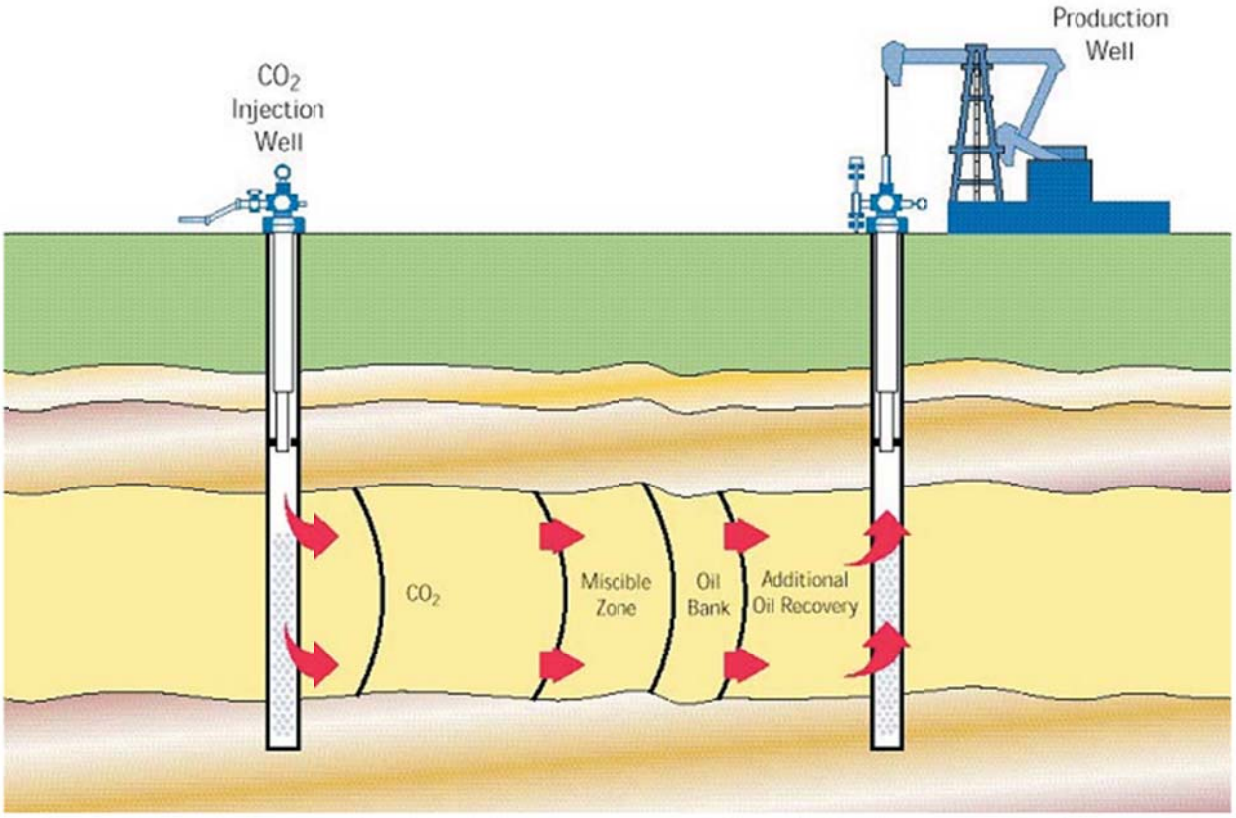

Figure 1.2: CO_2 enhanced oil recovery (Cano 2011)

1.2.3 Carbon Dioxide Conversion

Reduction of carbon dioxide from the atmosphere is very important whether by means of carbon capture and storage or by developing carbon free energy sources. Although the importance of these methods cannot be ignored but the more useful way to mitigate the carbon dioxide from the atmosphere is to capture it and convert it into useful products. There are several methods reported for the conversion of the carbon dioxide to other product including radiochemical method, thermo chemical method, photochemical method, biochemical method and electrochemical method. Among these processes reported, the reduction of carbon dioxide by electrochemical means offers several advantages over other processes provided that the electricity can be obtained from the renewable energy sources (Scibioh et al. 2004; Halmann et al. 1999).

1.3 Electrochemical Reduction of Carbon Dioxide

Electrochemical reduction of carbon dioxide is gaining remarkable attention in the scientific community these days. The advantage of this process includes the ambient reaction condition of temperature and pressure and the water can be used as the potential source of hydrogen ions (Halmann et al. 1999). Further, the range of the products can be obtained from the same raw materials (CO_2 and water) just by varying the electrode system and electrochemical conditions. There are several important adjustable parameters that affect the performances of the electrochemical reduction such as electrolyte, electrode catalyst or electrode system and the reaction conditions.

1.3.1 Role of Electrolyte

As indicated above, the solvent used in the reduction of carbon dioxide is usually water which is the basic reactant. Supporting electrolyte is usually added to enhance the ionic conductivity of the medium. During the early stage of the electrochemical CO_2 research, the effects of the supporting electrolyte were not studied. Later on it was identified that the supporting electrolytes used in this process not only increase the ionic conductivity but also play an important role in the reaction mechanism (Blajeni 1992). The electrolyte composition alters the solubility of the CO_2 in the electrolyte, affects the specific adsorption of the reactants mainly CO_2 and other intermediate species and ultimately the product distribution (Murata et al. 1991; Ikeda et al. 1987; Satoshi Kaneco et al. 1999).

Murata et al. (1991) studied the effect of alkali cationic specie on the electrochemical reduction carbon dioxide on Copper electrode at a constant current density of 5 mA/cm^2 with bicarbonate solution at a temperature of 18.5 ^oC with pH at electrode surface of 9.5. The production of hydrogen decreases in the order of Lithium (Li^+) > Sodium (Na^+) > Cesium (Cs^+)> Potassium (K^+), while the production of the hydrocarbon and alcohol remain highest with sodium and potassium ions. The effect of the cationic specie can be explained by the specific adsorption of the cation on the carbon dioxide and the intermediates. Cesium ion with the lowest hydration number being largest and softest among all these metal can easily adsorbed on the electrode surface and the potential recorded was the lowest i.e. more positive as shown in Table 1.1.

Table 1.1: Current efficiencies of the products in electrochemical reduction of CO_2 in 0.1M hydrogen carbonate solution (Murata et al. 1991).

		Faradaic Efficiencies (%)							
Cation	**Potential V/SHE**	**CH_4**	**C_2H_4**	**CO**	**EtOH**	**PrOH**	**$HCOO^-$**	**H_2**	**Total**
Li^+	-1.45	32.2	5.2	-	1.6	-	4.7	60.5	104.2
Na^+	-1.45	55.1	12.9	1.0	4.2	0.6	7.0	25.1	105.9
K^+	-1.39	32.0	30.3	0.5	10.9	1.6	8.3	14.5	98.1
Cs^+	-1.38	16.3	30.5	2.4	7.2	4.4	15.8	24.4	101.0

The effects of anionic specie have also been studied by Hori et al. (1989). They found that $KHCO_3$, KCl, $KClO_4$ and K_2SO_4 were more favorable for hydrocarbon formation while K_2HPO_4 promotes hydrogen evolution reaction. The reason is the neutralization of the OH^- by the HPO_4 ions at the electrode surface which favor more hydrogen evolution. Table 1.2 shows the effect of anionic species during the course of carbon dioxide reduction process with a pH being measured for bulk solutions after electrolyses (Hori et al. 1989).

Table 1.2: Faradaic efficiencies of product from the electro reduction of CO_2 at Cu electrode at 5mA/cm^2 in various solutions at 19 ^oC (Hori et al. 1989).

				Faradaic Efficiency (%)							
Electrolyte	**Conc. (mol/dm^3)**	**pH**	**Potential V / NHE**	**CH_4**	**C_2H_4**	**EtOH**	**PrOH**	**CO**	**$HCOO^-$**	**H_2**	**Total**
$KHCO_3$	0.1	6.8	-1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0
KCL	0.1	5.9	-1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
	0.5	-	-1.39	14.5	38.2	-	-	3.0	17.9	12.5	-
$KCLO_4$	0.1	5.9	-1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K_2SO_4	0.1	5.8	-1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K_2HPO_4	0.1	6.5	-1.23	17.0	1.8	0.7	-	1.3	5.3	72.4	98.5
	0.5	7.0	-1.17	6.6	1.0	0.6	0	1.0	4.2	83.3	96.7

1.3.2 Effect of Temperature and Pressure

The unique feature of electrochemical reduction of carbon dioxide is that it can be carried out at low temperature and pressure. However, there are significant effects on the variation of these operating parameters on the performance of the system. For example, the solubility of carbon dioxide in water increases with increasing pressure, resulting an enhanced reduction of CO_2 rate due to the availability of higher number of CO_2 molecule on the electrode (catalyst) surface. In the early literature, higher pressure was considered to achieve high reaction rate but later on higher currents with higher pressures were reported by other workers (Ryu et al. 1972; Kudo et al. 1993; Todoroki et al. 1995; Todoroki et al. 1995; Hara et al. 1997). Gas diffusion electrodes (GDE) are normally utilized in the fuel cell technology for many years but efforts have been made to use it for the carbon dioxide reduction process to overcome mass transfer problem (Mahmood et al. 1987; Furuya et al. 1997; Lee et al. 1999; Yamamoto 2002; Ikeda et al. 2009).

Unlike the pressure effects, the solubility of carbon dioxide decreases with increasing temperature (Duan et al. 2003). On the contrary, the current density of the carbon dioxide reduction increases with temperature. Ryu and his co-workers reported increase in current density of 20 times with increase in temperature from 275 to 333 K (Ryu et al. 1972). Köleli et al. 2004 carried out the reduction of carbon dioxide at higher temperature and higher pressure and he reported the increase in the faradaic efficiency of formate with increase in temperature from 298 to 353 K.

1.3.3 Electrode System and Catalysis

The conversion of carbon dioxide (either thermal or electrochemical) is high energy intensive given CO_2 is a very stable molecule. In case of electrochemical reduction of CO_2, the energy came from the electricity. It is possible to reduce carbon dioxide completely by applying higher potential. However, the incorporation of a suitable catalyst as elector significantly reduces the energy requirement and also the alter product selectivity. During the reduction of CO_2 in aqueous medium in addition to CO_2 reduction the electrolysis of water is also taken place that produces hydrogen. Therefore, in aqueous system there is always a competition between electrolysis and CO_2 reduction reaction in order to get more electrons and at the same time proton is needed to convert CO_2 to other products. On the other hand a suitable catalyst can minimize the water electrolysis reaction and enhances the CO_2 reduction reaction (Hori 2008). If the catalyst is going to reduce the amount of over potential then the energy required to carry out the reaction will decrease, it is called positive electro catalysis and which is desirable in our case (Scibioh et al. 2004). The selections of the proper electrode catalyst have been presented in the next chapter.

1.3.4 Use of Solid Electrolyte Polymer Membrane

The concept of using solid polymer electrolyte membrane provides the reduction of carbon dioxide in a gas phase directly thereby eliminating the mass transfer resistance. Suitable solid polymer electrolytes can be any ion conducting membrane usually hydrogen ions such as perfluorinated sulfonic acid copolymers including Nafion® 417

and Nafion® 117. The working electrode catalyst should be capable of reducing carbon dioxide which can be deposited by means of carbon materials on the cathode side of the membrane while the counter electrode used should be capable of producing hydrogen ion to be transported to the cathode side for the reduction reaction. The concept in explained by a schematic diagram in Figure 1.3. Reactions explained are expected with copper metal catalysts

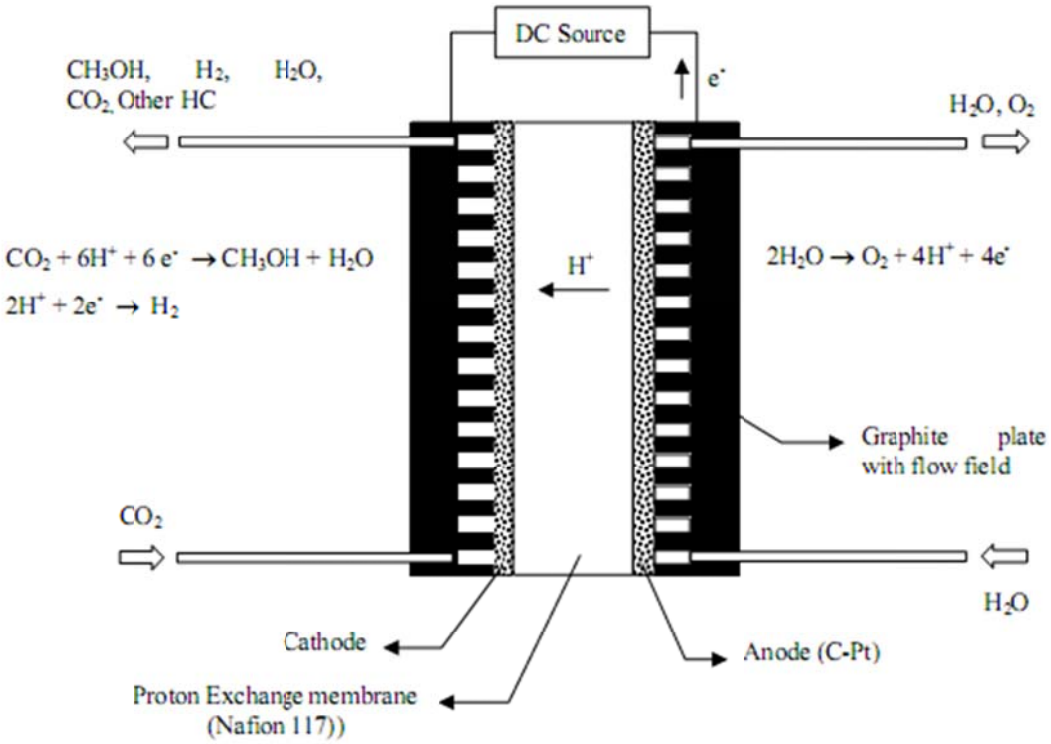

Figure 1.3 Schematic diagram of electrochemical reactor setup

Faradaic Efficiency

The performance of the electrochemical processes is usually evaluated in terms of faradaic efficiencies. The faradaic efficiency is defined as the fraction of the current passing through the cell that goes to the desired product or the charge used for producing the specific product divided by the charge passed through the cell during the experiment (Delacourt et al. 2008;Narayanan et al. 2011). The faradaic efficiency for the gaseous product can be calculated by the following expression:

$$F.E. = \frac{eFxF_m}{I}$$

Where

F.E. = Faradaic efficiency, e = no of electron exchanged, F = faraday's constant = 96487 C/mol, x = mol fraction of the gas, F_m = Molar flow rate

$$F_m = \frac{PF_v}{RT}$$

P = Pressure, F_v = Volumetric flow rate, R = Gas Constant, T = Temperature in Kelvin

Current Density

The current density is the measure of the electric current per unit area of the cross section. Higher current density at high faradaic efficiencies increases the importance of the carbon dioxide reduction process. Overall, it will be shown that electrochemical

systems that produce high faradaic efficiencies for highly reduced products and good current densities at modest electrode potentials remain a challenge.

Current density for the electrocatalytic reactions is analogous to the rate of the reaction for conventional heterogeneous catalytic system. In case of electrocatalytic systems, additional parameters such as potential (or voltage) and pH of the system comes into consideration. In addition to the reactant and product molecules, electrons or ions act as reactant and product. Figure 1.4 and Table 1.3 shows the comparison between the rate of reactions for conventional heterogeneous catalytic systems and electrocatalytic systems.

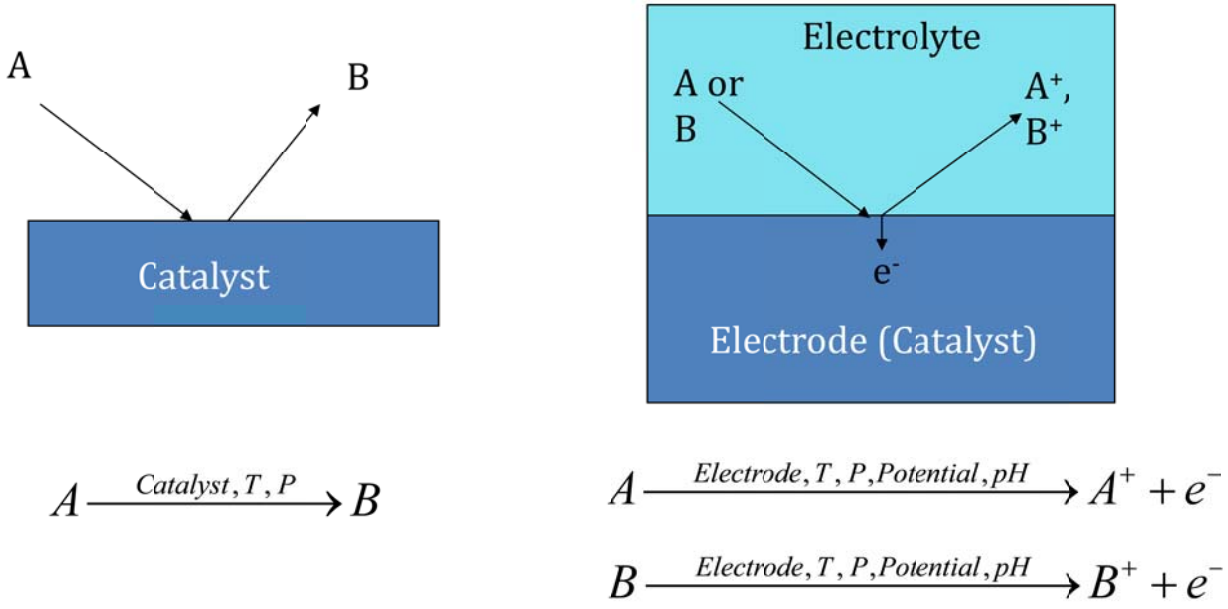

Figure 1.4: Comparison between heterogeneous and electrocatalytic reactions

Table 1.3: Unit comparison of heterogeneous and electrocatalytic reaction rates

Units of rate	
Moles/m^2s	*Moles/m^2s,* *Columbus/ m^2s* *or A/m^2 (Current Density)*

The faradaic efficiency of the electrochemical system is proportional to the amount of the product produced during the course of reaction. The overall conversion will be high if the total faradaic efficiency will be high, but the selectivity of the product depends on the faradaic efficiency of the specific product and it is inversely related to the current density.

In the present research, NiO and SnO_2 supported on MWCNT with different loading were prepared and evaluated in half cell. The selected catalyst was further evaluated in the electrochemical reactor which gave us CO and H_2 as the main products. The concentration of the product gases were obtained in ppm (v) level showing very low conversion of carbon dioxide and consequently low faradaic efficiencies. NiO /MWCNT catalyst showed promising results. The product selectivity and the faradaic efficiency can be enhanced by modifying the electrocatalyst and by controlling the experimental conditions and experimental setup.

Chapter 2

LITERATURE REVIEW

2.1 Background

Electrochemical reduction of carbon dioxide has been studied extensively over the last two decades and several review papers are available in the open literature (Jitaru et al. 1997; Scibioh et al. 2004; Gattrell et al. 2006; Jitaru 2007; Hori 2008; Li 2010). The process has been studied mostly in liquid phase two compartment cell separated by ion exchange membrane. Recently attempts have been made to reduce the carbon dioxide in the gas phase directly by utilizing the solid electrolyte conducting membrane (Nishimura et al. 1995;Hori 2003;Subramanian et al. 2006;Delacourt et al. 2008;Narayanan et al. 2011). Reduction of carbon dioxide leads to a variety of products from liquid products such as formic acid, methanol, ethanol and propanol to the gaseous products such as methane, ethane, and syngas. Carbon dioxide is a highly stable molecule and it is very challenging to convert it into other products. The type of the metal electrode, nature of electrolyte and the reaction parameters including pH, potential, temperature and pressure play an important role in the distribution of the product. Both aqueous (water) and non-aqueous (methanol) electrolyte have been tried to carry out the reduction reaction. Although importance of parameters mentioned above cannot be under estimated but the selection of the proper electrode system is the most important parameter (Jitaru 2007). In this chapter, the literature has been summarized on the basis of the type of metal

electrode used in the reduction process and the review based on the current methodology used in the process.

Reduction of carbon dioxide by electrochemical means offers several advantages over other processes such as radiochemical, biochemical and thermochemical method, since water can be used as an inexpensive reactant and reaction can be carried out at ambient conditions of temperature and pressure (Scibioh et al. 2004). Scibioh et al (2004) listed the reaction of carbon dioxide at thermodynamic potential. The reactions below show CO_2 reduction in aqueous solution at neutral pH at room temperature vs. Standard Hydrogen Electrode (SHE).

$$CO_2 + H^+ + 2e^- = HCCOH \quad (-0.61V)$$

$$CO_2 + 2\,H^+ + 2\,e^- = CO \quad (-0.52V)$$

$$CO_2 + 4\,H^+ + 4\,e^- = HCHO \quad (-0.48V)$$

$$CO_2 + 6\,H^+ + 6\,e^- = CH_3OH \quad (-0.38V)$$

$$CO_2 + 8\,H^+ + 8\,e^- = CH_4 \quad (-0.24V)$$

For an ideal system, carbon dioxide should be reduced to a specific product at a particular metal electrode at the thermodynamic potential as mentioned in the above equations. But in the real practice the more negative potential is usually required to carry out the reaction and this addition in the potential is known as the overpotential. More overpotential means more energy is required to carry out the reaction. The motivation of reducing carbon dioxide by electrochemical means comes from the fact that the Fischer

Tropsch synThesis or Sabatier process occurs at high temperature and high pressure which increases the cost of production, so to reduce CO_2 electrochemically at room temperature and pressure, the source of electricity should be from the renewable energy source. By this way the CO_2 concentration in the atmosphere will reduced otherwise, if electricity is producing from the burning of fossil fuels then the atmospheric CO_2 concentration will not be mitigated (Cole 2009).

The main focus of this Thesis is to study the activity of cathode suitable for CO_2 reduction so more emphasis will be on the electrode material in this chapter. The main challenge in the electrochemical reduction is to develop the procedure to reduce CO_2 with high faradaic efficiency and selectivity with high current densities.

2.2 Electrode System for CO_2 Reduction Process

Although the selectivity of the products obtained during the reduction of CO_2 process depends on various factors such as concentration of the reactants i.e. CO_2 and H_2O, potential applied to the electrode system, pressure and temperature as well as electrolyte solution if the reaction is carried out in aqueous phase. Among all these factors the selection of the metal electrode is the most important.

2.2.1 Classification of Metal Electrode

In the earlier literature of CO_2 reduction process , the metal electrodes were classified as sp and d group metals in the periodic table while later on it was found that the

classification do not hold significantly. Later on Hori (2008) has classified the metal electrodes into four groups based on the product selectivity (Hori 2008).

Formate Formation Metals

This group comprises of metals such as Pb, In, Sn, Cd, Tl, and Bi. The major product obtained from this group comprises of formate ion ($HCCO^-$).

CO Formation Metals and other inactive metals

This group comprises of Au, Ag, Zn e.t.c. the product obtained from these metals includes CO. With Ni, Fe, Pt, Ti e.t.c. the product comprise mainly of Hydrogen

Hydrocarbon Formation Metals

In this group, Cu is considered to the only metal which is highly selective for hydrocarbon product formation

Azuma et al. (1990) studied the reduction of carbon dioxide on various metal electrodes in low temperature $KHCO_3$ solution. They reported the reduction of carbon dioxide on 32 different metal electrodes at 0 ^oC. Hara et al. (1995) also reported the reduction of CO_2 on 32 different metal electrodes under high pressure in aqueous electrolyte.

Formate Formation Metals

During the reduction of carbon dioxide, the primarily reduction occurs to CO and HCOOH formation. The number of electron required to produce these two products is two. Formic acid is a very useful product and have received considerable attention due

its wide commercial application as an organic acid these days while CO due to its toxic nature is not generally desirable but can be useful if combines with H_2 which is collectively known as syngas.

Pb, In, Sn, Cd, Tl and Bi are found to be more selective to formate production. The production of formate / formic acid on these metal electrodes has been reported in the literature illustrated below.

Hori et al. (1985) investigated various metal electrodes in hydrogen carbonate solution for the reduction of carbon dioxide. In 0.5 M $KHCO_3$ Cd, Sn, Pb, and In were dominantly producing formate, with faradaic efficiencies having upper limits of 67.2 %, 65.5 %, 88.8 % and 97.6 % with the current density of 5.5 mA/cm^2 and the potential range from -1.66 V to -1.51 V vs. SHE (Hori et al. 1985).

Bandi (1990) presented the product efficiency of 78 % of formic acid with a composite electrode of Ruthenia and Titania with trace amount of silver for the reduction of carbon dioxide by electrochemical means (Bandi 1990).

Azuma et al. (1990) reported the formation of formic acid from Cd, In, Sn, Pb, Tl and Hg at -2.0 V and -2.2 V vs. SCE in 0.05 M $KHCO_3$ solution. They reported that the faradaic efficiency of the formate to be higher in low temperature solution electrolyte compare to room temperature of the electrolyte. The faradaic efficiency on Pb electrode was 8.6 % at room temperature while it increased up to 16.1 % at 0 ^oC. Similar analysis was carried out for other metals as well. The faradaic efficiency for formate remains highest in case of Hg electrode both at room temperature and low temperature with 87.6 % and 90.2 %.

Indium stands on the second with formate efficiency of 33.3 % and 70 %. Cadmium gives about 55.9 % while Tl and Sn are reported to be 53.4 % and 28.5 % at 0 ^{o}C (Azuma et al. 1990).

Hara et al. (1995) also showed the efficiency for formate production on Pb, Sn and In to be highest with the corresponding values of 95.5 %, 92.3 % and 90.1 % under high pressure with current density ranges from 163-200 mA/cm^2.

Furuya et al. (1997) investigated the CO_2 reduction process on gas diffusion electrodes consisting of Ru-Pd catalyst with a metal ratio of 1:1. Formic acid was the major product obtain with current density of 80 mA/cm^2 and a current efficiency of 90 % at -1.1 V vs. NHE (Furuya et al. 1997).

Spataru et al. (2003) reported the reduction of carbon dioxide on ruthenium dioxide deposited on boron doped diamond. Formic acid and the methanol were the main products with the product efficiencies of 40 % and 7.7 % in acidic and neutral media (Spataru et al. 2003).

Subramanian et al. (2006) reported the reduction of CO_2 to formate on a Pb electrode in an electrochemical membrane reactor with maximum current efficiency of 93 % with a formate concentration of 1.5 x 10^{-2} mol / dm^3. They used two different type of membrane including Nafion® 961 and Nafion® 430 as a solid electrolyte (Subramanian et al. 2006).

Innocent et al. (2008) reported the electroreduction of carbon dioxide with 65-90 % faradaic efficiency of formate in an aqueous medium in a filter press cell. Potential of -

1.6 V vs. SCE with a pH range of 7-9 was found to be more appropriate with a supporting electrolyte solution of 0.5 mol/L NaOH (Innocent et al. 2008).

Kwon et al. (2010) reported the formic acid formation on nano layered Pb electrode from CO_2 reduction with 94.1 % faradaic efficiency on a cubic Pb surface (Kwon et al. 2010).

Narayanan et al. (2011) reported the conversion of carbon dioxide in an alkaline polymer electrolyte membrane with Lead and Indium electrode. They demonstrated the instantaneous faradaic efficiencies of up to 80% of formate production while over the time the Faradaic efficiency decreases. De-ionized water, sodium carbonate as well as sodium bicarbonate solution were studied as electrolyte.

Machunda et al. (2011) reported the reduction of carbon dioxide on Sn based gas diffusion electrode with 18 % faradaic efficiency of formate after initial 5 min chronoamperometric analysis while decreases up to 12 % at the end of the experiment after 1 hr (Machunda et al. 2011).

CO Formation and other Non Active Metals

Reduction of carbon dioxide to carbon monoxide has been observed with Ag and Au metals mostly in the literature.

Hori et al. (1985) reported the faradaic efficiencies of 89.9 % and 93 % on these metals with a current density of 5.0 mA/cm^2 at a potential range of -1.14 V to -1.45 V vs. SHE. Zn was also reported to produce 63.3 % faradaic efficiency with current density of 5.5 mA/cm^2 at -1.56 V vs. SHE. Metals such as Fe, Cu, In, Cd, Sn also produced CO but the

values were very low as compared to Ag, Au and Zn. Nickel was found to be inactive for CO production under the same condition (Hori et al. 1985).

Azuma et al (1990) found the current efficiency of 40.7 % at 0 ^{o}C while 30 % at room temperature at -2.2 V vs. SCE in 0.05 M $KHCO_3$ solution at Ag electrode while with Au it was 16.9 % at 0 ^{o}C. Ni, although considered as inactive for CO formation produces CO with 40.7 % faradaic efficiency when the temperature was went down to 0 ^{o}C. Palladium, Copper and Titanium were also reported to produce CO at 0 ^{o}C (Azuma et al. 1990).

Kudo et al. (1993) investigated that the carbon dioxide reduction on Ni electrode at the ambient pressure does not significantly produces hydrocarbon and other useful products while on increasing pressure the reaction products were mainly CO, formate and methane. The faradaic efficiencies of CO increased from 0% to 10.4%, for HCCOH it increased from 0.1% to 23.2% and incase of methane it increased from 0.62% to 1.78% respectively on increasing pressure from 1 atm to 60 atm (Kudo et al. 1993).

Under high pressure of 30 atm, Hara et al. (1995) extensively studied CO_2 reduction on various metal electrodes. It was found that those metals which are not considered as active for CO production at atmospheric pressure showed significant improvement in the faradaic efficiency at high pressure. Nickel and Palladium reduced CO_2 with faradaic efficiencies for CO to be 33.5 % and 46.1 % with a current density of 163 mA/cm^2 in 0.1 M $KHCO_3$ solution at a potential ranges from -1.56 V to -1.59 V vs. Ag/AgCl reference

electrode. Ag and Au remained on top with faradaic efficiencies of 75.6 % and 64.7 % while Zn produced CO with 48.7 % efficiency (Hara et al. 1995).

Kedzierzawski et al. (1994) reported the reduction of carbon dioxide on gold electrode in 0.1 $NaHCO_3$. The faradaic efficiency of CO production was 93.4 % at -0.955 V vs. NHE and decreases up to 28.7 % on increasing more negative voltage till -1.45 V (Kedzierzawski et al. 1994).

Kaneco et al. (1998) reported the reduction of carbon dioxide to carbon monoxide and formic acid on Ag electrode at low temperature in KOH and methanol electrolyte. They studied the effect of low temperature. The efficiency for CO formation increases with increasing more negative potential but with decreasing temperature while the current efficiency for H_2 formation increase with increasing temperature (Kaneco et al. 1998).

Yano et al. (2002) studied the reduction of carbon dioxide on Ag electrodes at two and three phase interfaces. In case of liquid and solid phase electrolysis the conversion of CO_2 to CO was reported with faradaic efficiency of 65 % but decreases as the electrolysis time increases. In case of three phase system i.e. solid, liquid and gas phase interface, the faradaic efficiency of CO was reported to be 45 % while faradaic efficiency of hydrogen was reported to be very low up to 8 % (Yano et al. 2002b)

Hori et al. (2003) investigated the reduction of carbon dioxide on silver coated ion exchange membrane with 0.2 M K_2SO_4 electrolyte. The faradaic efficiency of 74.4 % and 62.7 % were reported at a current density of 20 and 50 mA/cm^2 for CO production. The voltage was measured as -1.49 V and -1.80 V vs. SCE (Hori 2003).

Delacourt et al. (2008) studied the reduction of carbon dioxide on reverse fuel cell approach using Ag and Au supported and unsupported catalyst. Both Nafion membrane and catholyte layer inserted Nafion membrane were used to carry out the reaction. Various designs of electrochemical cell were discussed. Carbon monoxide and hydrogen were obtained at a current density of 80 mA/cm^2 and potential of -2.0 V vs. SCE (Delacourt et al. 2008).

Hydrocarbon Formation Metals

Yoshio Hori is considered as the pioneer to report the reduction of carbon dioxide to hydrocarbon in aqueous electrolyte on copper electrode in hydrogen carbonate solution (Hori et al. 1985; Hori et al. 1986). The faradaic efficiency for methane formation was reported to be 65% at 0 ^oC while it decreases on increasing temperature. The efficiency was reported to be negligible while the faradaic efficiency for ethylene was increasing on increasing temperature with a current density of 5 mA/cm^2 at a potential range of -1.33 to -1.39 V vs. SHE in 0.5 M $KHCO_3$ solution electrolyte.

Cook et al. (1987) reported the reduction of carbon dioxide to methane with higher current density of 38 mA/cm^2 with faradaic efficiency of 33 % at a potential of -2.29 V vs. SCE (Cook et al. 1987).

Cook et al. (1988) investigated insitu electrodeposited copper for carbon dioxide reduction on glassy carbon electrodes in aqueous 0.5 M $KHCO_3$. The faradaic efficiencies of 73 % , 70 % and 68 % for CH_4 and 25 %, 15% and 11 % for ethylene at a current density of 8.3 mA/cm^2, 16.7 mA/cm^2 and 25.0 mA/cm^2 respectively. The

mechanism was proposed that methane and ethylene are not formed due to the direct electrochemical reduction of CO_2 and involves some intermediate steps (Cook et al. 1988).

De Wulf et al. (1989) further reported the reduction of CO_2 to methane and ethylene in aqueous alkaline solution at Cu electrode at a potential of -2.0 V vs. SCE. They studied the methane and ethylene faradaic efficiencies at 0 ^oC, 26 ^oC and 48 ^oC. Current efficiency for methane formation was decreased with increasing the temperature but the current was 15 times more in case of 26^oC as compared to 0 ^oC, while at 48 ^oC the current increase was about 1.5 times higher than that at 26 ^oC. With the increase in temperature the ethylene efficiency was significantly increased while methane was observed to be very low (DeWulf et al. 1989).

Hori et al. (1989) reported the reduction of carbon dioxide on copper electrode in aqueous solution to different hydrocarbon products such as CO, hydrocarbon gases and alcohol products at room temperature. The effect of supporting electrolyte and potential were studied. The production of CO was more prominent at less negative potential around -1.2 V vs. NHE and the production of other hydrocarbons were favored below -1.3 V vs. NHE. Formation of ethylene and the alcohol was reported to be more favorable in KCl, K_2SO_4, $KClO_4$ while bicarbonate alkaline electrolyte was more suitable for methane production (Hori et al. 1989).

Mizuno et al. (1995) reported the reduction of carbon dioxide in methanol at -30 ^oC to methane, carbon monoxide and ethylene. The maximum faradaic efficiency for methane

formation was 42.5 % at a potential of -2.0 V vs. SCE. For CO at a potential of -1.8 V vs. SCE, faradaic efficiency of 12 % was obtained. Very low faradaic efficiency 2.1% of ethylene was obtained at a temperature of -30 ^{o}C (Mizuno et al. 1995).

Yano et al. (2002) studied the reduction of carbon dioxide on a Cu electrode to CO, CH_4 and C_2H_4 in an acidic medium. The conversion of carbon dioxide to CO and C_2H_4 in KCl acidic medium was reported to be 30 % (Yano et al. 2002a)

Kaneco et al. (2006) studied the reduction of carbon dioxide on copper electrode to ethylene using potassium and rubidium hydroxide as the supporting electrolytes. The faradaic efficiency of ethylene was found to be 37.5 % at a potential of -4.0 V vs. Ag/AgCl in KOH / methanol mixture. The maximum current efficiency for ethylene in case of RbOH / methanol mixture was 30 % at a potential of -4.0 V vs. Ag/AgCl electrode (Kaneco et al. 2006).

Yano et al. (2007) investigated the pulse mode electrochemical reduction of carbon dioxide and Cu and copper oxide electrodes. The maximum faradaic efficiency for CH_4 formation was found to be 33.3 % in 0.1 M $KHCO_3$ supporting electrolyte (Yano et al. 2006).

Chang et al. (2009) studied the reduction of carbon dioxide on Cu_2O catalyzed carbon clothes. The study was carried out to observe the effect of catalyst in inert and CO_2 electrolyte solution. (Chang et al. 2009).

Le et al. (2011) reported the formation of methanol from electrochemical carbon dioxide reduction at copper oxide electrodes. The current efficiency for methanol was found to be 38 % (Le et al. 2011).

2.3 Problem Statement and Scope of Work

The comprehensive literature review reveals that ERC can be carried out using variety of electrode surfaces. The reduction of carbon dioxide has mostly studied using solvent electrolyte system with bulk metal as cathodic material i.e. catalyst. During the ERC, there are numbers of competitive chemical reactions occurs at the same time on the surface of the electrode. The product distributions are primarily depending on the type of electrode material (catalyst) and the nature of the electrolytic solution. The electrolyte solution determines the concentration and stability of the reactants and the products formed during reactions. The current density and electrode potentials are the key parameters during any electrolytic process. Generally, appreciable CO_2 reduction rate can be obtained if the current density is high at the low electrode potential.

Reduction potential and product selectivity for electrochemical carbon dioxide reduction process are most important parameters. Attention is needed in order to reduce carbon dioxide with high current efficiencies providing minimum electrode potential. So the main challenge associated with carbon dioxide reduction process includes: (1) to get high selectivity of the hydrocarbon products (2) to use an electrode that produces hydrocarbons with maximum current efficiency with minimum electrode potential. Other parameters like type of electrolyte, and pH of the medium also affect the reaction mechanism.

The reduction of CO_2 requires a source of energy and this energy is provided with the help of electricity in the electrochemical reduction process. So to develop an efficient

catalyst and lowering the over potential at a cost of getting higher current density has been considered to be the key for a successful implementation of the carbon dioxide reduction process. Mass transfer resistance in the aqueous electrolyte solution is also a concern given the low solubility of CO_2. In this regard, introduction of solid electrolyte membrane can be an interesting alternative to minimize the mass transfer limitations. In open literature there are only limited numbers of research articles reporting the development of the solid electrolyte membrane based systems. Most of the earlier works used nafion membrane which is acidic. On the other hand, the carbon dioxide reduction process is more favorable in the alkaline medium. Therefore, there are tremendous opportunities of developing alkaline membranes suitable for electrochemical reduction of CO_2 processes.

As per the catalyst, bulk metals are mainly studied. On the other hand, supported metal catalysts shows superior performances in most of the catalytic processes. Therefore, there is scope of developing supported catalysts using different metals/support combinations.

The present research is focused on the development on the electrocatalyst. In this regard carbon nanotubes has been considered as the potential support material given its high surface area, superior strength, nano scale structure and other properties favorable as support material. To best of our knowledge the carbon nanotubes as a support material in the carbon dioxide reduction process have not been reported so far. As per the metals, NiO and SnO_2 are considered because of their proven catalytic performance, abundant availability and low price compare to the other candidate materials.

Chapter 3

OBJECTIVES

The main objective of this research is to develop supported nickel oxide (NiO) and tin oxide (SnO_2) based catalysts suitable for the electrochemical reduction of carbon dioxide. In order to obtain high dispersion of the active component (NiO and SnO_2), high surface area multi walled carbon nanotubes (MWCNT) are used as support material.

The following are the specific objectives of this research:

i. Preparation of NiO and SnO_2 catalysts supported on multi walled carbon nanotubes with different metal oxide contents.

ii. Characterization of the NiO /MWCNT and SnO_2/MWCNT catalyst samples using X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques.

iii. Electrochemical evaluation of the catalysts in a half cell reaction set up and to study the effect of the metal oxide content on the current density of the reaction system using electrochemical techniques such as linear sweep voltammetry (LSV) and chronoamperometry (CA).

iv. Electrochemical evaluation of the selected catalyst in the electrochemical reactor similar to reverse fuel cell reaction setup.

Chapter 4

EXPERIMENTAL

4.1 Experimental Plan

Keeping in view the objective of the study, the most fundamental step to start the work is to develop the experimental plan. In this study we have planned to develop the supported catalyst which is based on the carbon nanotubes materials with NiO and SnO_2 being the active component. Different loading of NiO and SnO_2 to be incorporated in the CNT matrix was done by impregnation technique. Then characterization techniques such as XRD, SEM and EDX were employed to study the morphology and crystalline size of the active component. Electrochemical evaluations of the prepared catalysts were studied with the help of LSV and CA. The electrochemical study was first carried out in a half cell to screen the catalyst among all the loaded catalyst prepared. The best loading catalyst was further evaluated in the electrochemical reactor similar to reverse fuel cell and the product was analyzed using gas chromatography techniques.

Given below is the explanation of the experimental techniques employed in this study followed by the experimental procedure.

4.2 Methods

The following experimental techniques have been employed to carry out this research

- Dry Impregnation Method for catalyst preparation

- X-ray Diffraction (XRD) for catalyst characterization
- Scanning Electron Microscopy (SEM) for catalyst characterization
- Energy Dispersive X-ray Spectroscopy (EDX) for catalyst characterization
- Linear Sweep Voltammetry (LSV) for catalyst evaluation/screening
- Chronoamperometry (CA) for catalyst performance test in ECR

4.2.1 Dry Impregnation Method

Impregnation methods are usually employed for the preparation of the heterogeneous catalysts. The metal precursor is usually dissolved in the aqueous phase. The amount of the water to be used is equal to the volume of the pores of the support material. The advantage of dry impregnation method includes the ease in control of the weight of the metal added while the dispersion obtained may not be as good as obtained from other synThesis methods. The maximum amount of the loading is usually determined by the solubility of the precursor in the solution (Ross 2011).

4.2.2 X-ray Diffraction

The X-ray diffraction is a technique employed to get the useful information about the phase identification and the crystal structure of the material. It is based on the constructive interference of monochromatic X-rays and a crystalline sample. The main component of the X-ray diffractometer includes the X-ray tube, sample holder and the X-ray detector. The X-ray diffractometer are equipped with the computers. Smart Lab

(9 kW) Rigaku XRD diffractometer was used to carry out the experimental analysis. The principle being the generation of the X-ray in a cathode ray tube to produce electron by filament heating, then the voltage is applied to accelerate the electrons towards the sample and the bombardment of the electrons and the material takes place. X-rays intensity is recorded as the sample and the detector rotates (SERC 2011).

4.2.3 Scanning Electron Microscopy

Scanning electron microscopy techniques is used to get the highly magnified image of the samples. Sample includes catalyst powders, polymer or the surface of the metals. Normally images are taken at some specific part of the sample to be desired. The principle is the focusing of beam of high energy electrons to generate the variety of signals at the solid surface or powder surface. SEM assembly generally includes electron source, electron lenses, detectors and the display units. Prior to taking image samples are put in the holder and are coated with the gold. The reason is that the specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. The electrically conducting material, deposited on the sample is either by low-vacuum sputter coating or by high-vacuum evaporation. Besides gold coating other Conductive materials in current use for specimen coating include , platinum, osmium, iridium, tungsten, chromium (SERC 2011).

4.2.4 Linear Sweep Voltammetry

Linear sweep voltammetry is the voltammetric technique in which the potential or voltage applied to the working electrode varies linearly with time. The response of the current is to be measured while varying the potential between working electrode and reference electrode in a three electrode system. A scan rate in a unit of mV/sec can be fixed from low to higher values. The technique is usually employed to study the performance of the electrochemical systems.

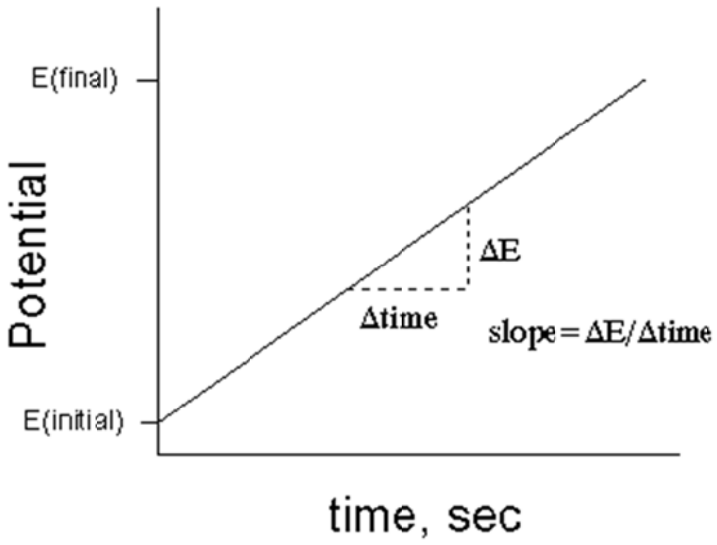

Figure.4.1: Linear sweep voltammetry (LSV) curve.

4.2.5 Chronoamperometry

Chronoamperometry is an electrochemical technique in which the potential or voltage of the working electrode system is fixed at some value and the system is allowed to run for the specified period of time and the response of the current is measured. It is steady state analysis give useful information about the electrochemical behavior of the system.

4.3 Experimental Procedure

The section is divided in to the following sub sections

- Catalyst preparation
- Catalyst characterization
- Electrochemical evaluation

4.3.1 Catalyst Preparation

In this investigation the high surface area NiO/MWCNT and SnO_2/MWCNT electrocatalysts were prepared by incipient wetness technique. The functionalized MWCNT's obtained from Cheap Tubes Inc. USA were used as a support material while $Ni(NO_3)_2 \cdot 6H_2O$ and $SnCl_2$ from Sigma Aldrich Co LLC Germany was used as nickel and tin precursor. For catalyst preparation, the calculated amount of salt precursor was first dissolved in de-ionized water and allowed the solution for sonicating for few minutes. Once the solution was ready, then it was impregnated in MWCNT support. In case of tin precursor tiny drop of HCl was added to expect SnO_2 instead of SnO. The resulting

slurry was subjected to sonication for another two hours in order to obtain a homogeneous solid solution. Then the samples were dried in an oven at 110 ^{o}C for 24 hours followed by the calcinations steps which were carried out in a tubular furnace in an argon atmosphere for 3 hours at 450 ^{o}C to decompose the nitrates. Following the after mentioned procedure different NiO/MWCNT and SnO_2/MWCNT catalyst samples were prepared with metal oxide loading of 10, 20, 30 and 40 weight percent.

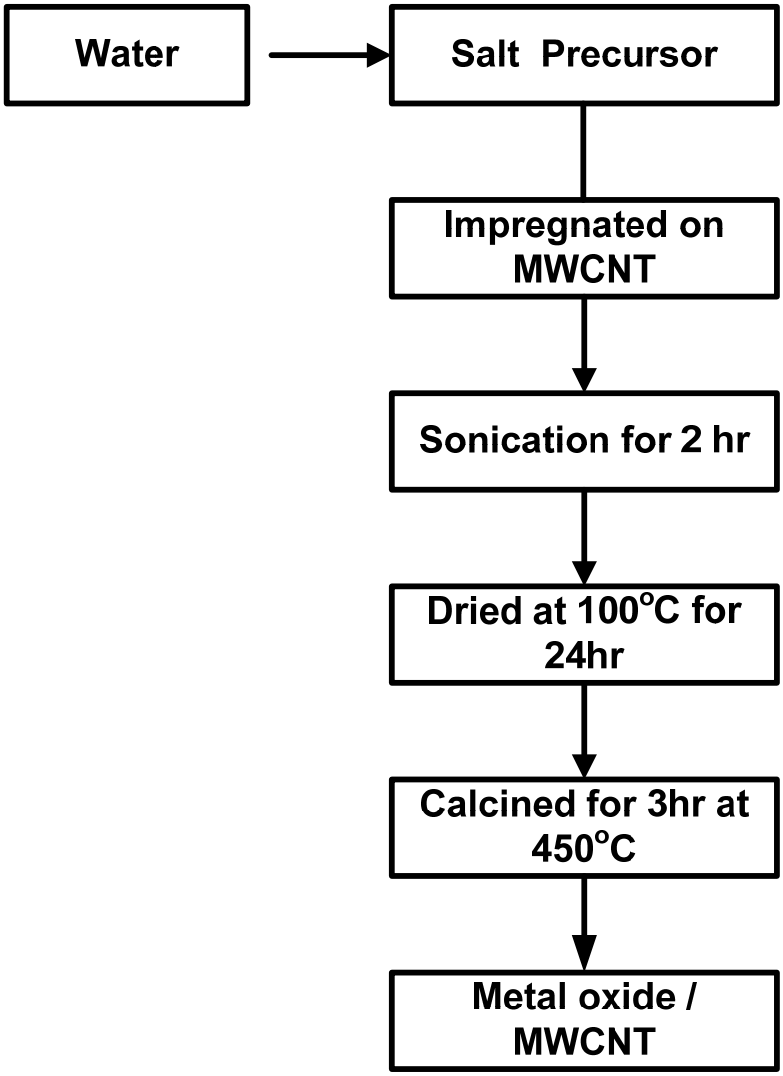

Figure.4.2: Catalyst preparation steps

4.3.2 Catalyst Characterization

The prepared NiO/MWCNT and SnO_2/MWCNT catalysts with different loadings were characterized using different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX).

Surface structure of the prepared catalysts was obtained by using a JEOL JSM-6460LV SEM. The catalyst powders were grounded and then adhered onto the surface of the sample holder using double sided copper tape. The samples were then sputter coated with gold using ion sputter. The scale bar is shown on each of the SEM pictures. The size of the particle was also calculated. The quantitative analysis of the catalyst particles were conducted by using the Energy-Dispersive X-ray system (EDX) that was incorporated in the SEM instrument.

The diffraction pattern of NiO and SnO_2 on MWCNT was acquired by using the Smart Lab (9 kW) Rigaku XRD diffractometer, with Cu-Kα radiation. The catalyst particles were ground into powder and loaded onto a sample holder. Diffraction data were collected between 10 to 70^o 2θ and the JCPS powder diffraction database was used for XRD patterns identification. The crystal size of samples was measured by using well known Scherrer's equation.

$$d = \frac{K\lambda}{B\cos\theta}$$

Where B is the width of the XRD pattern line at half peak height (radian), λ is the wavelength of the X-ray (nm), θ is the angle between the incident and diffracted beams (^{o}) and d is the crystal size of the powder sample (nm).

4.3.3 Electrochemical Evaluation

The electrochemical analysis was carried out in the half cell and the electrochemical reactor.

4.3.3.1 Half Cell

Figure 4.7 shows the schematic diagram of a half cell (H-cell) used in this study. The H-cell is a two compartment cell separated by ion exchange membrane. A three electrode system was used to carry out linear sweep voltammetry (LSV) and chronoamperometry (CA) measurements with the help of autolab potentistat PG 102 as shown in Figure 4.8.

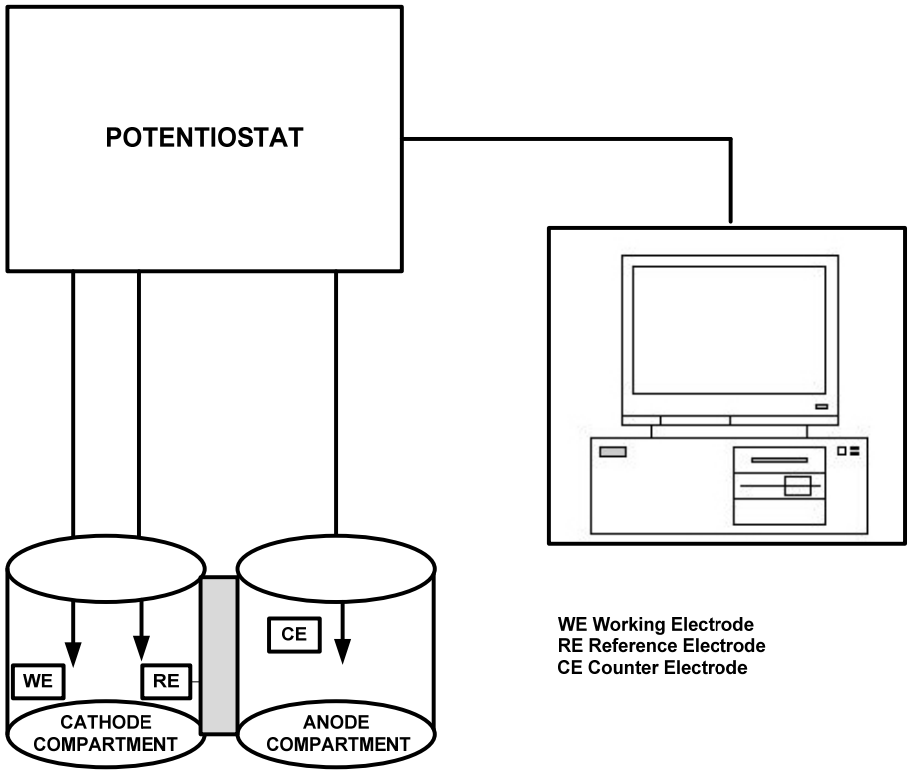

Figure.4.3: Half cell reaction setup

Electrolyte Preparation

Molar solution of $NaHCO_3$ was prepared using de-ionized water. $NaHCO_3$ was obtained from Lobachemi, India. 84 gm of $NaHCO_3$ powder was first dissolved in de-ionized water and then transferred to 2000 ml volumetric flask. The flask was shook well to get the homogeneous solution. De-ionized water was obtained from Milli-Q Advantage A10 ultrapure water purification system obtained from Millipore, Italy.

Electrode Preparation

Working electrode

Cathode is playing a role of working electrode. Carbon paper strip was used to prepare working electrode. Carbon strip used was completely covered with Teflon tape except the area where the catalyst powder was deposited. Catalyst deposition was done by sonicating 30 mg catalyst powder in a mixture of water and propanol while Nafion® solution (5 wt% Nafion®, in isopropanol) was added as a binder. The uniform slurry was pasted on a 2050-A carbon paper of 1 cm^2 area with the help of paint brush. The catalyst was loaded by keeping carbon paper on a hot plate maintaining at approximately 80 ^oC. The catalyst was added as layer by layer and finally dried in an oven for 10 min at 100 ^oC to remove the moisture content.

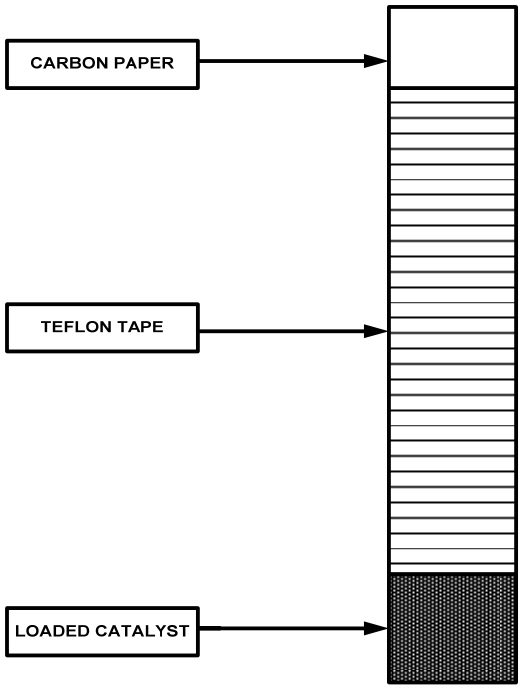

Figure 4.4: Working electrode

Counter Electrode

Anode is working as a counter electrode. The platinum mesh was used as a counter electrode. The area of the counter electrode is higher than the working electrode.

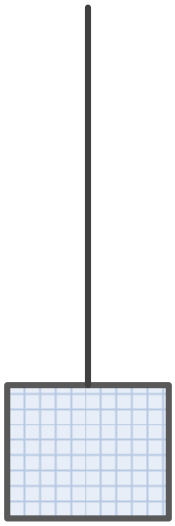

Figure 4.5: Counter electrode (Pt-mesh)

Reference Electrode

Saturated calomel electrode (SCE) is used as a reference electrode.

Cell Setup

The catholyte compartment was first purged with N_2 in order to remove the dissolved O_2 and to make the system inert. The CO_2 was flow in the same compartment for 30 minutes to saturate the solution. Carbon paper loaded with catalyst was then immersed in the cell. The reference electrode was also placed with the help of Luggin capillary. Counter electrode was placed in the anolyte compartment. The potential was applied with a scan rate of 50 mV/s and the response of current was measured for LSV. The same reaction was also carried out in an inert atmosphere. For CA the fixed amount of voltage was applied and the response of current was measured for 3000 seconds.

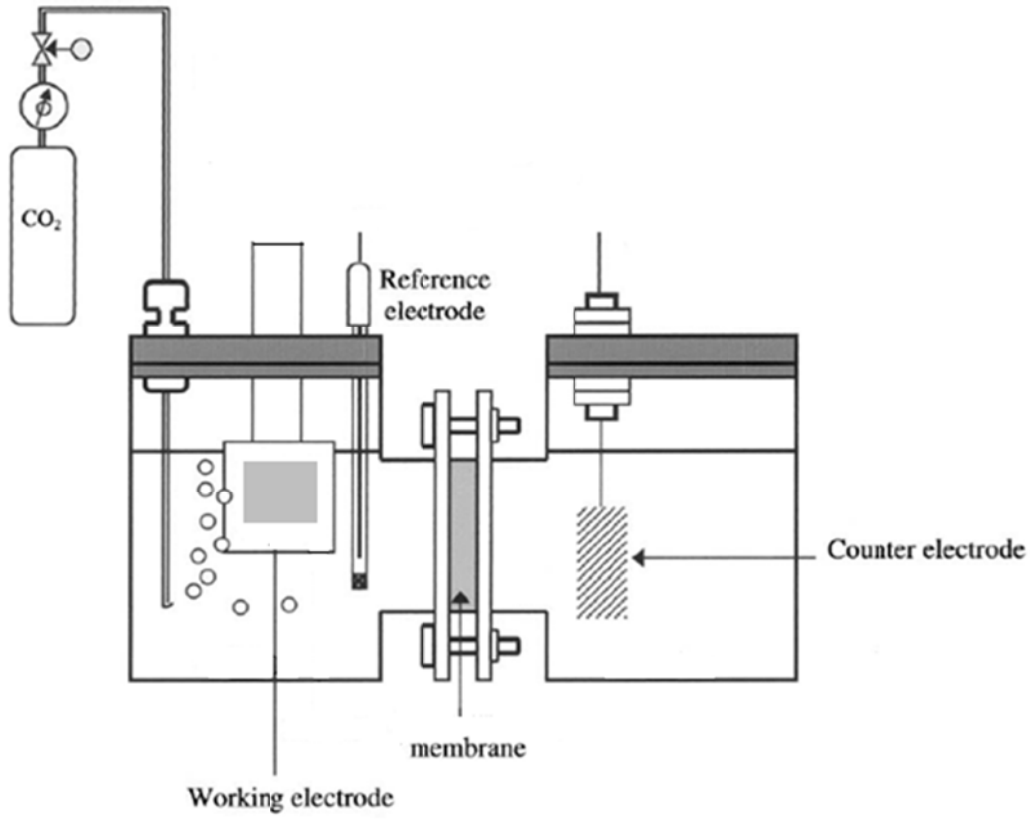

Figure 4.6: Half Cell

4.3.3.2 Electrochemical Reactor

Figure 4.14 and Figure 4.15 shows the picture and schematic diagram of an electrochemical reactor used in this study. Electrochemical reactor is nothing but a reverse fuel cell reactor. Cathode and anode compartments are separated by membrane electrode assembly (MEA) and the catholyte layer was inserted between the cathode catalyst and the membrane.

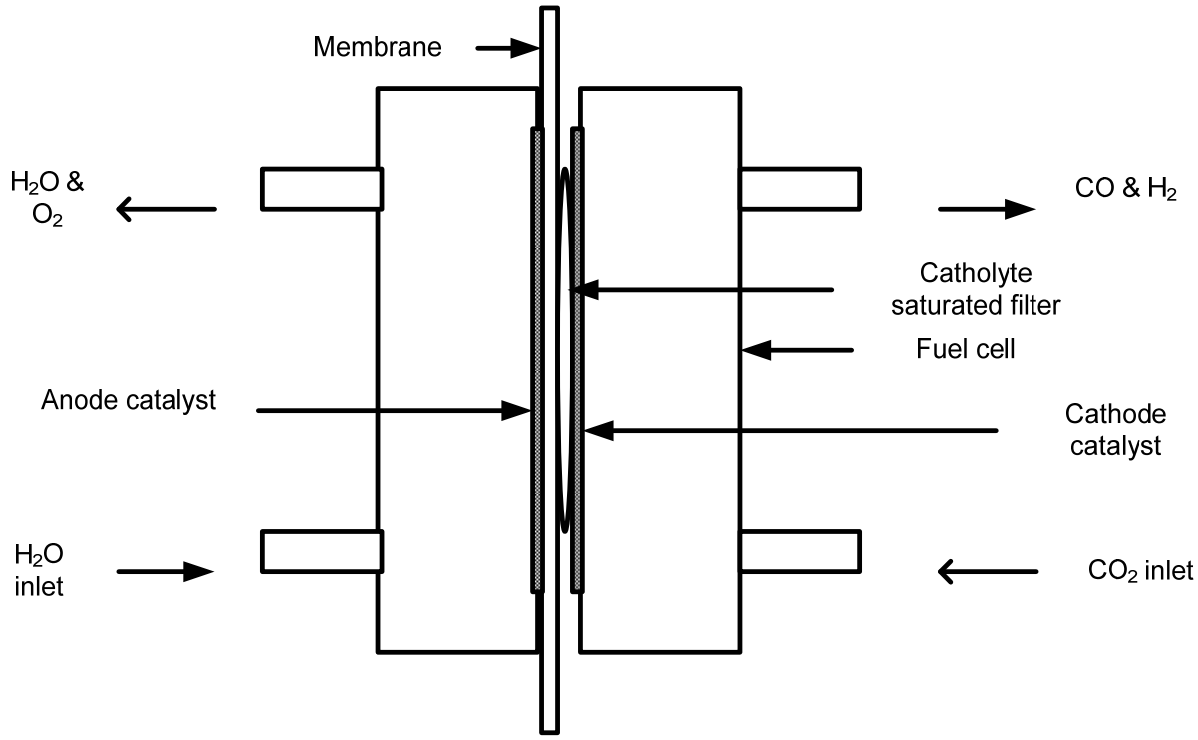

Figure 4.7: Schematic diagram of reverse fuel cell

Electrolyte

Nafion® 117CS ion exchange membrane obtained from Fuel Cell Store, USA was used as a solid electrolyte. The cathode and anode deposited on carbon paper was sandwiched between this Nafion® membrane by hot pressing at 130 ^{o}C and 1000 psi for 5 min. Nafion® membrane is acidic in nature while reduction of CO_2 is more favorable in basic medium. So a layer of catholyte rich in alkaline medium was inserted between membrane and the cathode catalyst. Whatman GF/D of 2.7 μm pore size was used for this purpose. Delacourt et al. (2008) modify the fuel cell setup by inserting the same catholyte (alkaline) layer of glass fiber Whatman GF/D of 2.7 μm pore size saturated with bicarbonate solution (Delacourt et al. 2008). We have also inserted the same catholyte layer to study the case.

Electrode Preparation

Cathode is playing a role of working electrode. Its preparation involves the sonication of catalyst powder 500 mg in a mixture of water and propanol while Nafion® solution (5 wt% Nafion®, in isopropanol) was added as a binder. The uniform slurry was pasted on a 2050-A carbon paper of 25 cm^2 area which was acquired earlier from Fuel Cell Store, USA. The catalyst was loaded by keeping carbon paper on a hot plate maintaining at approximately 80 ^{o}C. The catalyst was added as layer by layer and finally dried in an oven for 10 min at 100 ^{o}C to remove the moisture content.

Anode is working as a counter electrode. 60% Pt-Ru/C commercial catalyst obtained from E-Tek was used as a counter electrode. The loading procedure is same as cathode side.

Cell setup

The membrane electrode assembly was prepared by sandwiching the cathode and anode catalyst loaded on carbon paper between the Nafion membranes. In the modified setup, the glass fiber soaked with 0.5 M $NaHCO_3$ was inserted between the cathode catalyst and the membrane. The CO_2 with a flow rate of 20 mL/min at room temperature and atmospheric pressure was supplied to the cathode side of the fuel cell. Prior to entering the cell the gas was passed through the hydrocarbon trap in order to remove any impurity present in the gas and to humidifier to humidify gas. The flow of CO_2 was controlled by means of mass flow controller. De-ionized water was circulated on the anode side of the cell with the help of peristaltic pump. The potential was applied and the current was measured.

Product Analysis

The gaseous product from the cathode line was directly injected into the GC–TCD analyzer. The gas analysis was carried out using GC TCD detector. The column was specially designed for the detection of hydrocarbon material.

Chapter 5

RESULTS AND DISCUSSION

This chapter presents the characterization and electrochemical results of both the prepared NiO/MWCNT and SnO_2/MWCNT catalysts. As mentioned in the Chapter 4, XRD, SEM and EDX were employed to characterize all the catalyst materials. The promising catalysts were selected based on characterization and linear sweep voltammetry (LSV) tests. Finally, selective catalysts were evaluated using an electrochemical reactor using pure CO_2 as reducing gas.

5.1 XRD

NiO/MWCNT

Figure 5.1 shows the X-ray diffraction patterns of different NiO/MWCNT catalyst synthesized with various NiO loadings. It can be noted from this Figure that all the catalyst samples show similar XRD pattern which indicates presence of same metal oxide phases at different metal loaded catalysts. The first peak at 26^o corresponds to carbon while the other two peaks at 37^o and 43^o are NiO (111) and NiO (200), respectively (Azadi et al. 2010). These results are in good agreement with that available in literature (Afanasov et al. 2011; Chen et al. 2011; Liao et al. 2009; Lota et al. 2011; Loc et al. 2006; Qiu et al. 2009; Woointranont et al. 2011; Wu et al. 2004) and available library of the XRD instrument. Apparently the height of the first peak is increased with increasing the nickel loading on the MWCNT support. This is an indication of larger nickel crystals

size at higher metal loading. In order to ascertain the fact, the NiO crystalline size was also calculated using Scherrer's equation and is shown in the Figure 5.2. The nickel oxide crystallites become larger at higher loadings of NiO, resulting in poor dispersion and this can be seen in the SEM images as well. Similar phenomenon has also been observed in other literature as well (Azadi et al. 2010).

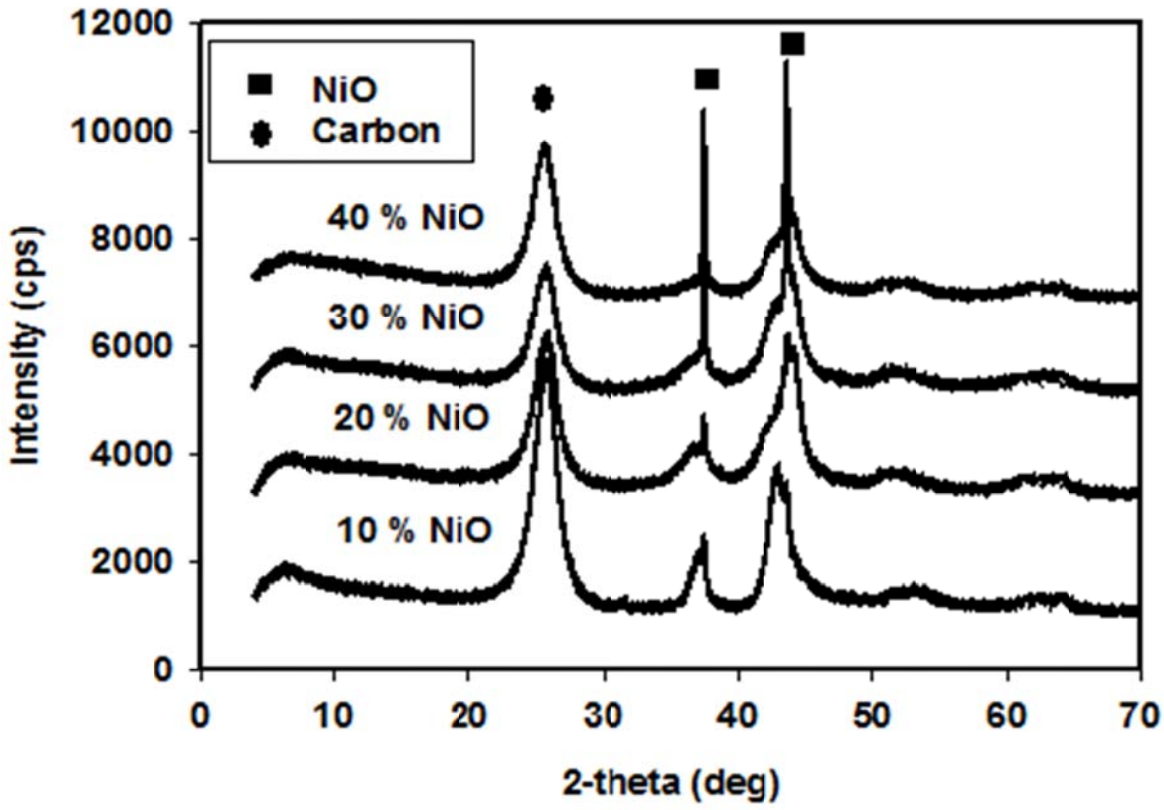

Figure 5.1: XRD pattern of NiO/MWCNT catalyst

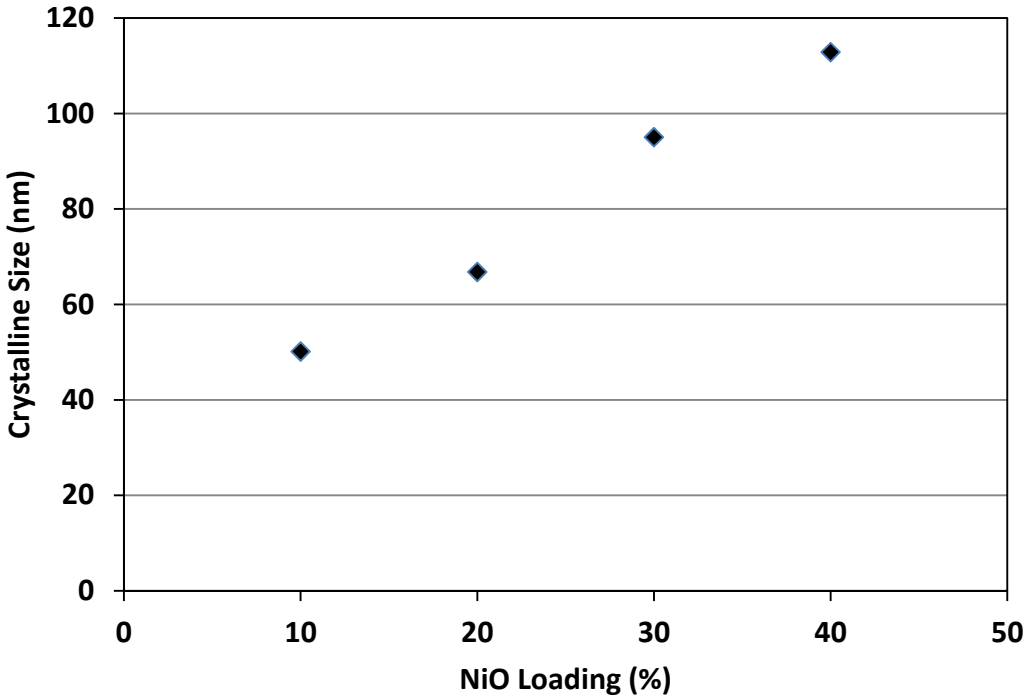

Figure 5.2: Crystalline size of NiO with different loading

XRD analysis of SnO_2/MWCNT catalyst has also been carried out. Figure 5.3 shows the XRD pattern of 20 % SnO_2/MWCNT catalyst. Different crystalline phases of SnO_2/MWCNT catalyst have been obtained. SnO_2 phase of (110) at two theta angle of 26.63º overlaps with carbon peak (002). Besides this several other peaks of SnO_2 have been observed at 2 theta angle of 33.90 º, 38.23º, 42.80º, 51.77º, 54.67º, 64.59º and 78.73º. These results are in good agreement with that available in literature (Fu et al. 2009;Xie et al. 2005;Du et al. 2010;Hsu et al. 2010) and available library of the XRD

instrument. The SnO_2 crystalline size was also calculated using Scherrer's equation and is found to be 31.5 nm corresponding to the peak having high intensity.

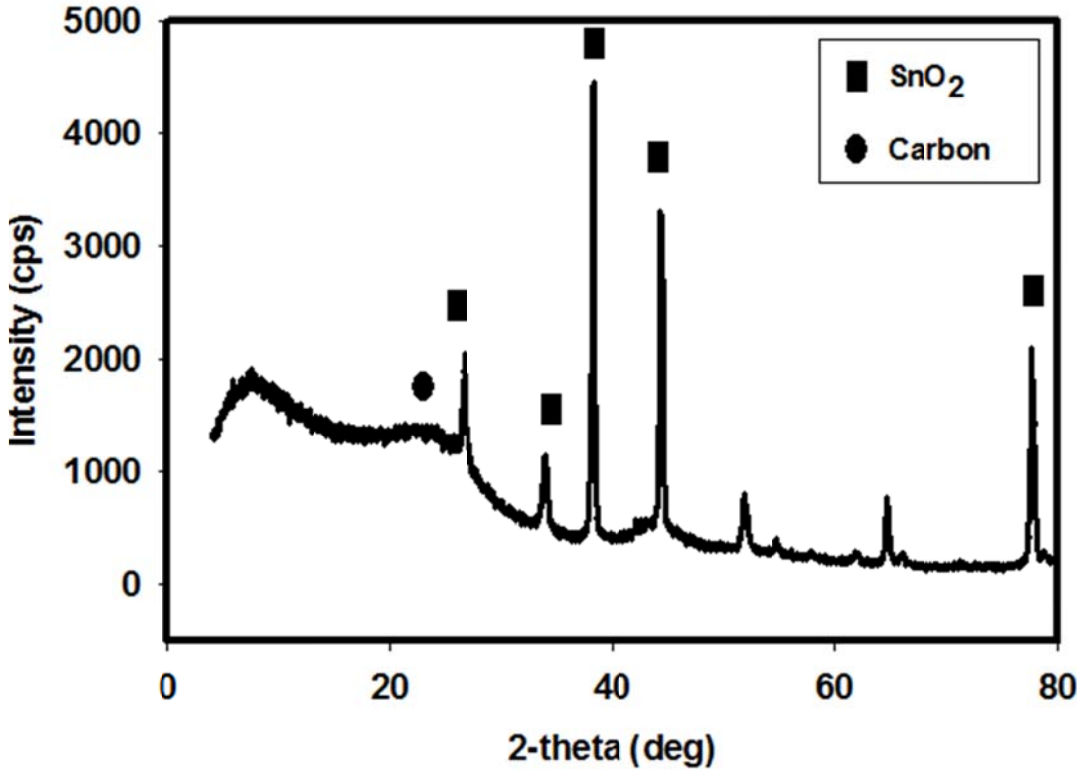

Figure 5.3: XRD of 20 % SnO_2/MWCNT

5.2 SEM

SEM results of NiO/MWCNT shown in Figure 5.4 and 5.5 were very much consistent with the XRD plots of NiO on MWCNT. As the metal oxide content was increased the crystalline size increases and as a result the dispersion went down. SEM was carried out with magnification x16000 at 1μm scale.

Quantitative analysis of the NiO/MWCNT catalysts samples were also carried out using EDX attached on the SEM equipment. Table 5.1 and 5.2 shows the result of 20 % NiO/MWCNT and 40 % NiO/MWCNT. The results were close to the actual values with error of 5.123 % in case of 20 % loading and 6.04 % in case of 40 % loading. The actual loading is always reported to be lower than the nominated one. Zangouei et al. (2010) reported different nickel loading on alumina and actual content was different than the amount used (Zangouei et al. 2010).

SEM image of 20 % SnO_2/MWCNT is also shown in Figure 5.6. The SnO_2 content is uniformly dispersed on the carbon nanotubes matrix.

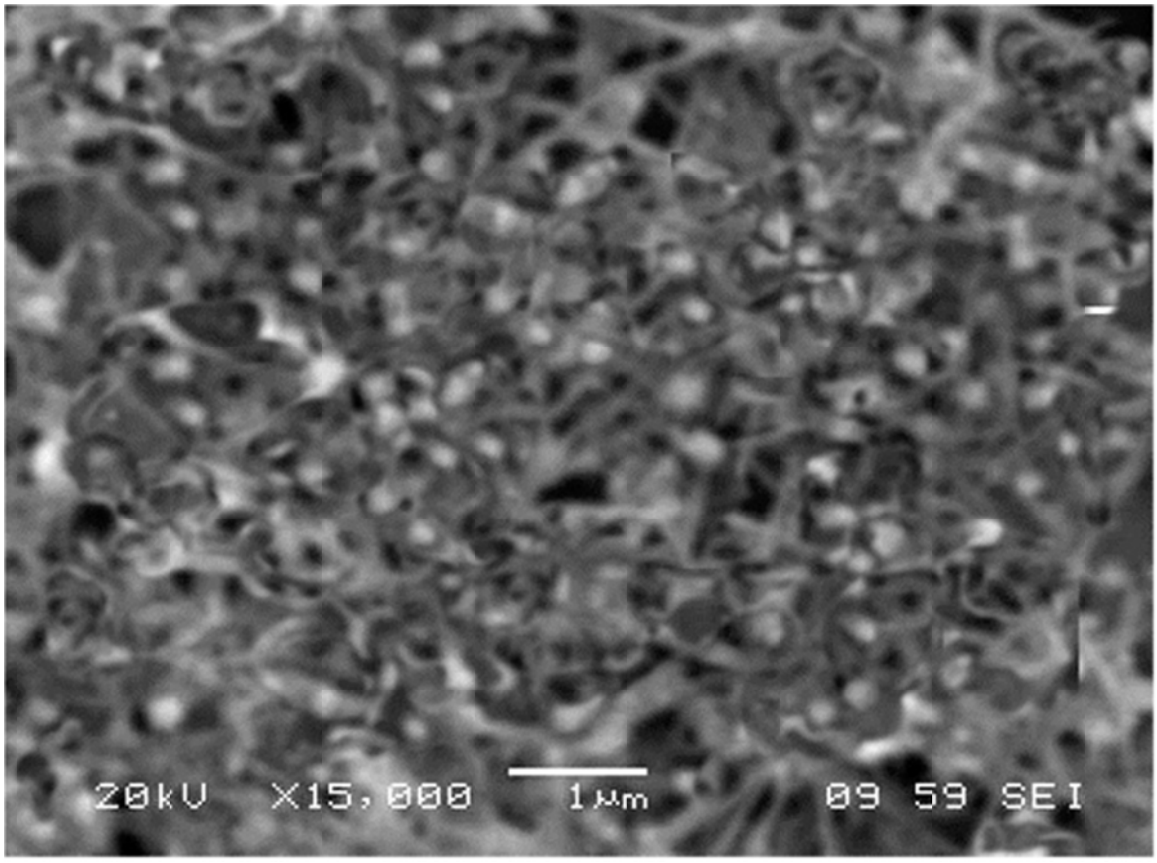

Figure 5.4: SEM image of 20% NiO/MWCNT

Table 5.1: Elemental analysis of 20 % NiO/MWCNT

Element	**Weight percent (%)**
C	81.1
O	4.87
Ni	14.02
Totals	100

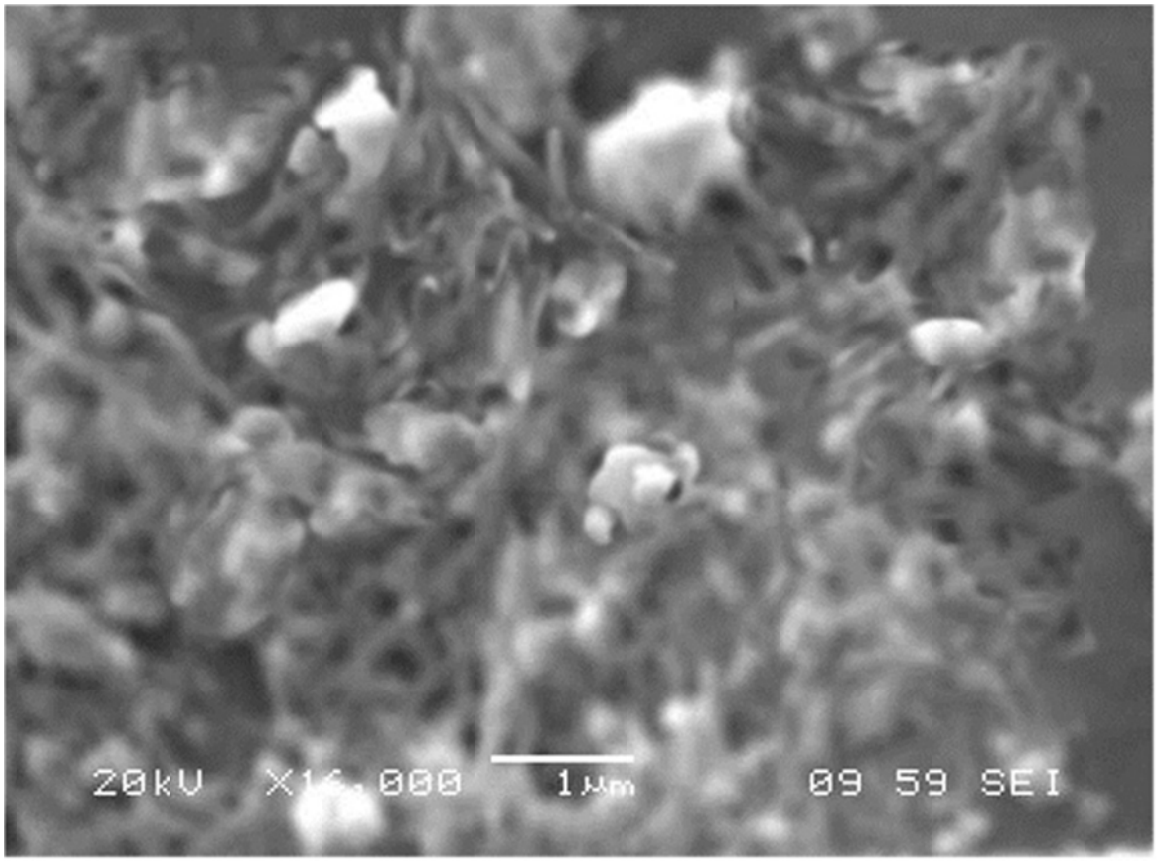

Figure 5.5: SEM image of 40% NiO/MWCNT

Table 5.2: Elemental analysis for 40% NiO/ MWCNT

Element	**Weight percent (%)**
C	62.9
O	8.27
Ni	28.83
Totals	100

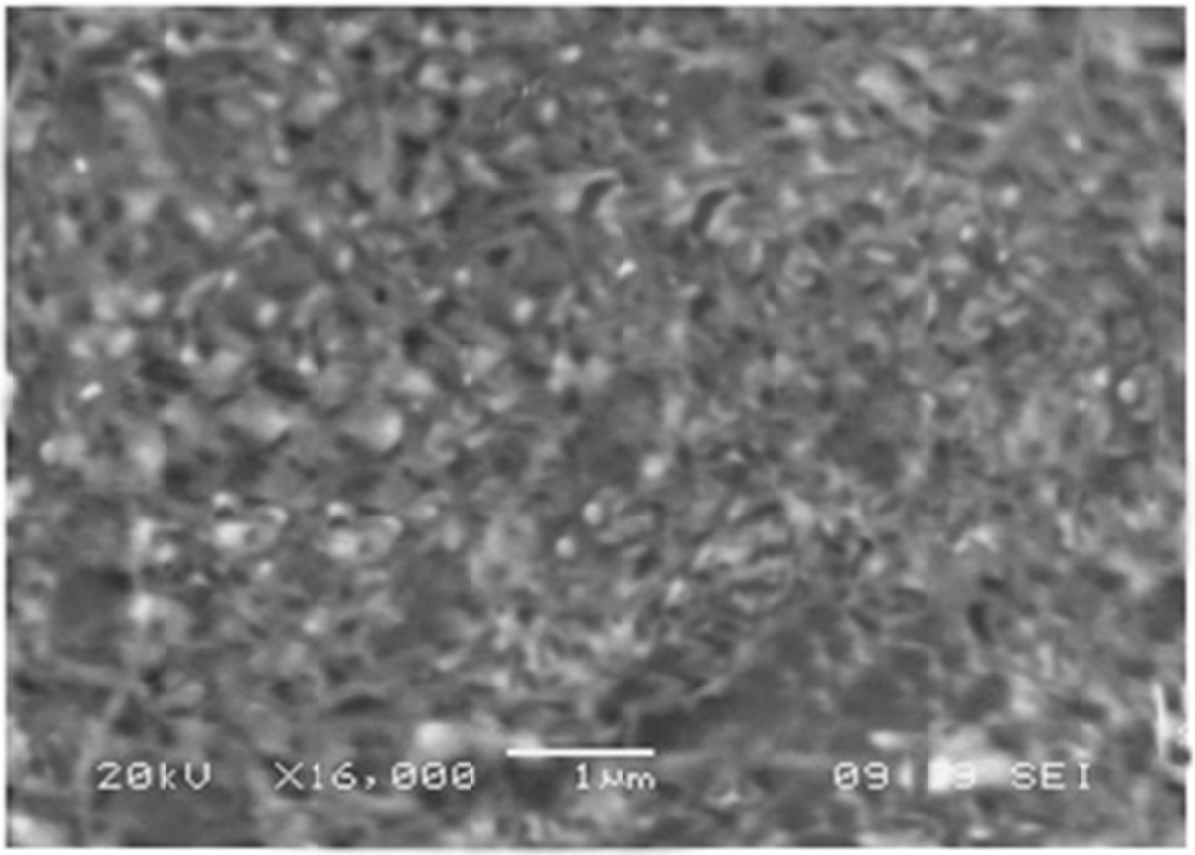

Figure 5.6: SEM image of 20 % SnO_2/MWCNT

5.3 Linear Sweep Voltammetry and Chronoamperometry

Figure 5.7 and Fig 5.8 show the LSV curve during the CO_2 reduction with different amount of nickel and tin loaded on MWCNT catalyst as electrode. NiO/NWCNT and SnO_2/MWCNT with various metal oxide loading (10 %, 20 %, 30 % and 40 %) were evaluated using CO_2 saturated solution. The optimum NiO and SnO_2 loading for the reduction of CO_2 in the electrochemical cell was obtained using LSV experiments. The parameter used to find the best catalyst was the current density. Current density for electro catalytic reactions is indicator of rate of reaction. For all catalysts the reduction of carbon dioxide was assumed to be more at the higher voltages. However, the hydrogen production competes during this reduction process and the energy consumption on hydrogen evolution reaction becomes more prominent with further increase of the voltage. For example, the thermodynamic equilibrium potential for methane formation is -0.25V vs. NHE (Normal Hydrogen Electrode) while for hydrogen formation it is -0.41V vs. NHE (Normal Hydrogen Electrode). Although in actual practice these reactions occurs at high negative voltages and this increase in potential is known as over potential. So it is very difficult to conclude that the amount of potential applied will results in CO_2 reduction. Even, it might be possible that the entire potential ended up with H_2 production (W. Li 2010). To get higher current with minimum over potential remains the big challenge for scientist while dealing with CO_2 reduction process. In order to identify the catalyst producing the higher current LSV technique was applied and using both active CO_2 and inert N_2 saturated solution as the electrolytic medium.

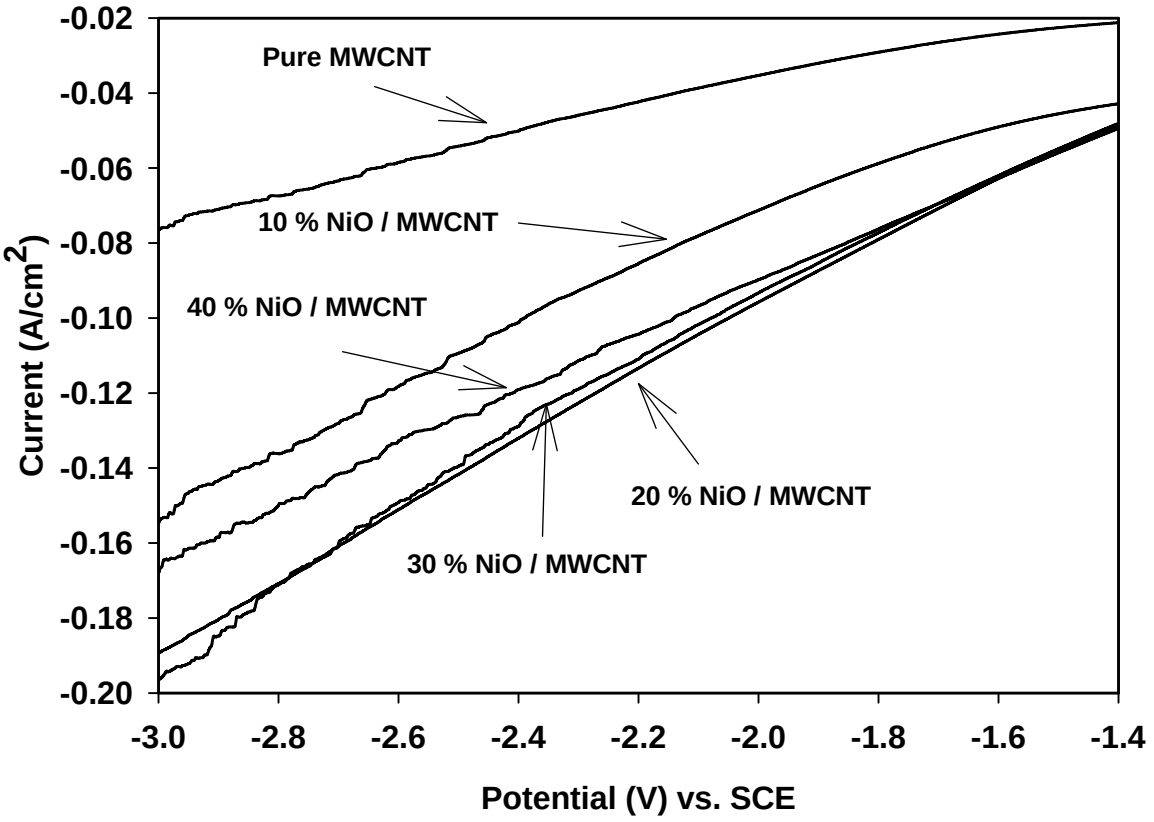

Figure 5.7: LSV measurements of different NiO/MWCNT catalysts in 0.5M $NaHCO_3$ solution saturated with CO_2

It is clear from the Figure 5.7 that the optimum loading of NiO is found to be 20 % at different voltages vs. SCE (Saturated Calomel Electrode). The optimal parameter being the total amount of current produced. The catalyst with 30 % NiO shows a slight increased in current measurement to that was obtained using 20 % NiO loaded catalyst. Further increase of NiO to 40 % starts decreasing the current. This observation is consistent to the catalyst characterization results described above. As seen earlier in XRD analysis, the crystalline size of NiO particle was increased with the increase of the NiO content. Therefore the NiO bigger crystals behave like bulk metal and the surface area available for the reaction starts decreasing so the reaction rate was low as compared to 20 % NiO content. This phenomenon can be further illustrated through our SEM analysis, the dispersion of the NiO particles on MWCNT was poor in case of higher loading and size of the particles were very large so we can say that 20 % NiO was found to be best for the reduction of carbon dioxide among the given samples prepared. Similar analysis was carried out with SnO_2/MWCNT catalyst as well as shown in Figure 5.8 and optimum loading obtained in this case is also 20 % SnO_2 supported on carbon nanotubes and the similar explanation can be done with this catalyst as well.

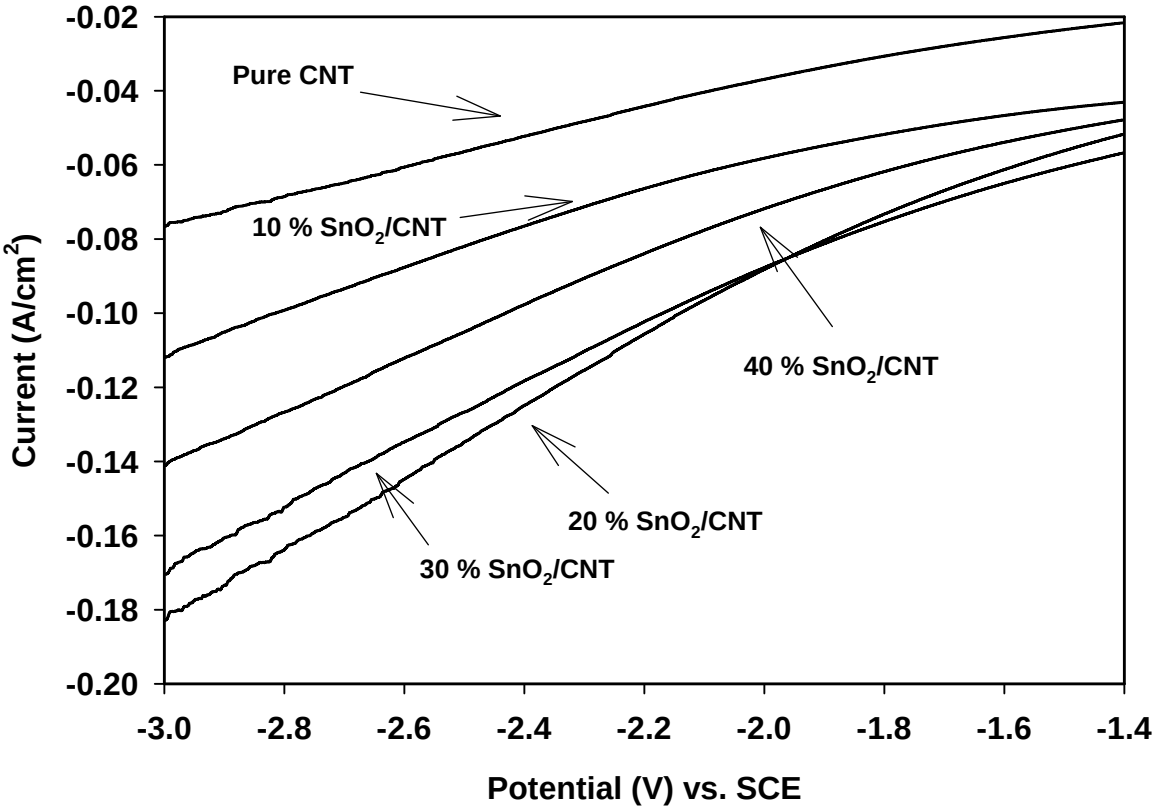

Figure 5.8: LSV measurements of different SnO_2/MWCNT catalysts in 0.5M $NaHCO_3$ solution saturated with CO_2

Since reduction of carbon dioxide in aqueous electrolyte proceed in parallel with hydrogen evolution reaction, it is important to identify whether the contribution of the catalytic effects in producing current by the reduction of the carbon dioxide rather than due to the hydrogen evolution reaction. In order to ascertain this, the reactions were carried out in the aqueous electrolyte using CO_2 saturated solution and N_2 saturated inert solution. The difference in the current between the two determines the actual amount of current produced due to the electrochemical reduction of CO_2.

Figure 5.9 to Figure 5.11 compares the LSV curves using N_2 and CO_2 saturated solution for 10 %, 20 %, and 30 % NiO/MWCNT catalysts.

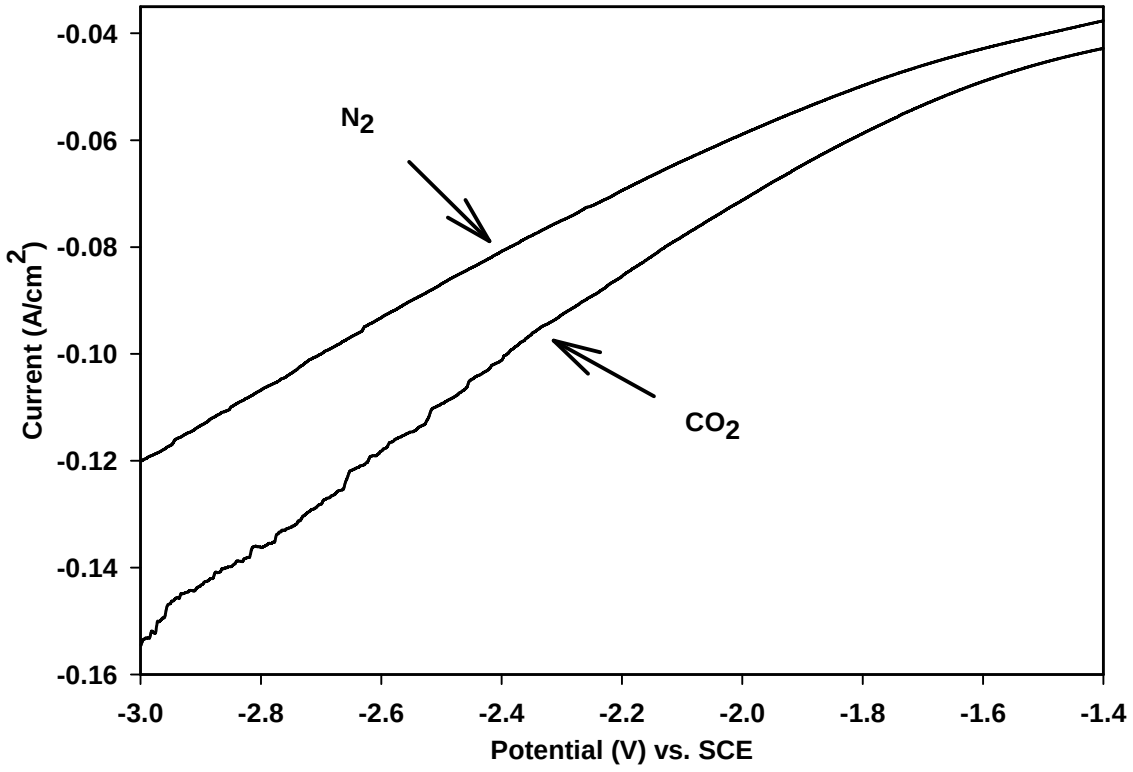

Figure 5.9: LSV measurement of 10% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution

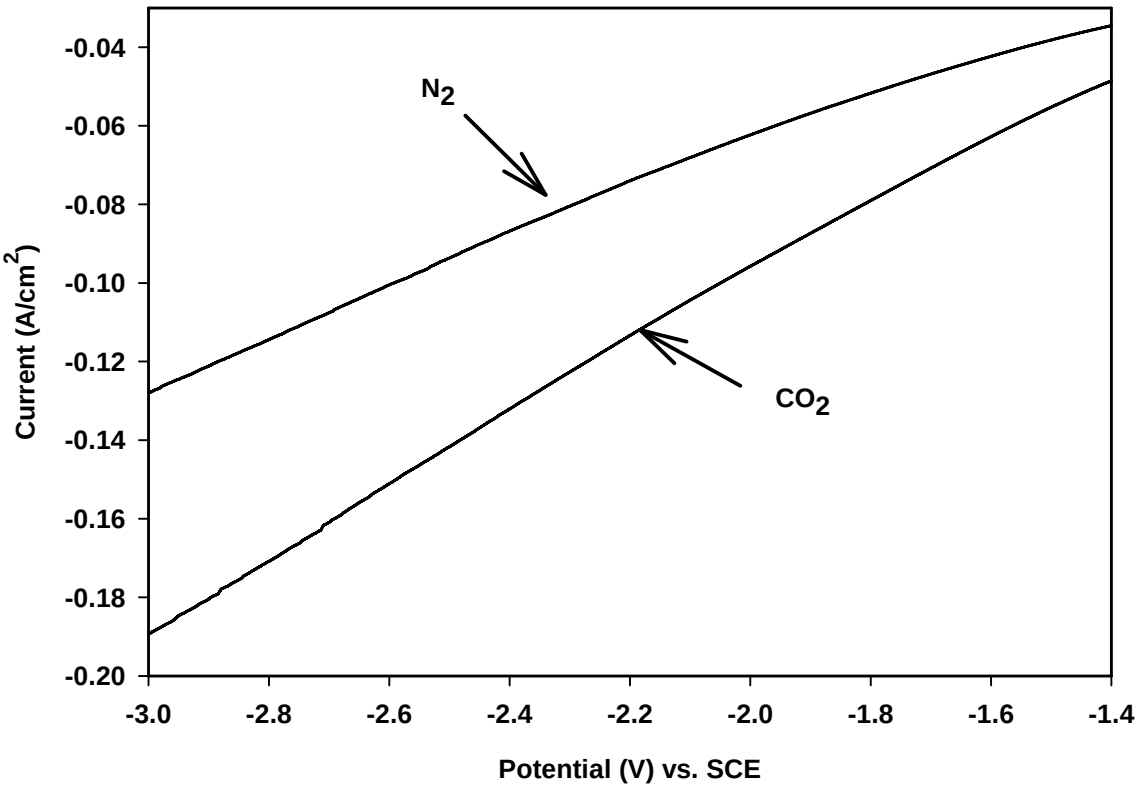

Figure 5.10: LSV measurement of 20% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution

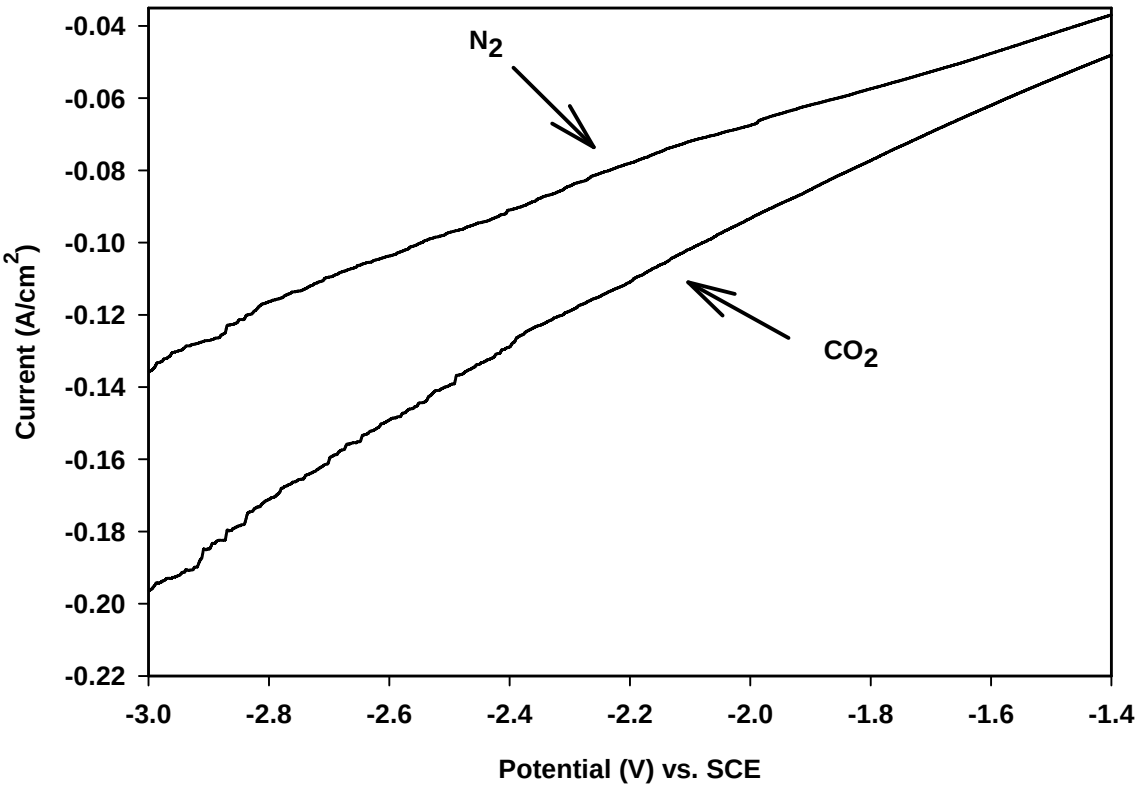

Figure 5.11: LSV measurement of 30% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution

It is important to highlight here that the amount of current obtained in CO_2 saturated solution is higher than that obtained in N_2 saturated solution. The observed higher current with CO_2 saturated solution is in line with some of the findings that are available in the open literature. However, there are some reports suggested that the amount of current obtained from the CO_2 is lower than that in the N_2 saturated solution. It was believed that CO, produced initially during the course of electrochemical reduction of CO_2 adsorbed on the Ni surface which suppressed the hydrogen evolution reaction, consequently the CO_2 shows lower current that those were found using N_2. In case of the present study the higher current was possibly due to the presence of the MWCNT as support materials. For further confirmation, the experiments were repeated several times and ended up with the same results. After careful investigation it was hypothesized that the use of CNT as a support material in the reduction of carbon dioxide plays a vital role in the reaction intermediate. Kudo.et.al (1993) carried out the electrochemical reduction of carbon dioxide at high pressure on Ni electrodes and reported the lower current at atmospheric pressure in CO_2 saturated solution. However, at elevated pressure the current was increased as compared to the atmospheric conditions. Therefore in the context of the present research it was considered that the MWCNT produces nano scale effect which we were calling here as high pressure effect at normal pressure which happens to occur due to nano scale dimensions of carbon nanotubes used and the nano scale pore dimensions; so the amount of current obtained with CO_2 saturated solution is higher than in N_2 solution. Imai et al. (1991) demonstrated that the pores having width of less than 2 nm encounters with enhanced physical adsorption by overlapping surface field

leading to the high pressure reaction conditions at normal pressure and called it micropores effect which is analogous to nano scale effect. Yamamoto et al. (2000) reported similar effects using micropores activated carbon fibers that lead to the similar high pressure effect at normal pressure.

As mentioned earlier, the LSV is a useful tool for quick analysis and ranking the catalyst activity for the reduction reaction. For more reliable and long term analysis, Chronoamperometry (CA) was performed. Basically CA is a steady state analysis that shows the actual current calculation for the series of catalyst for long period of time. In these experiments the current response was observed for 3000 sec at the voltage of -1.7 V vs. SCE reference electrode. The potential was selected given the objective is to reduce the carbon dioxide at minimum possible applied voltage. As mentioned earlier, although high voltage is favorable for the reduction of CO_2 it also leads to more hydrogen evolution reaction.

Figure 5.12 shows the CA analysis of NiO/MWCNT with different NiO loadings. In case 30 % nickel oxide catalyst the current slightly higher than that of 20 % NiO loaded catalyst. Given the difference is not that significant, it was considered that 20 % nickel oxide on MWCNT is the optimum loading. Figure 5.13 shows the CA analysis of SnO_2/MWCNT catalysts. The 20 % tin oxide loading is giving the higher rate of reaction i.e. higher current density. The analysis was also carried out N_2 saturated and CO_2 saturated solution for NiO/MWCNT catalysts and the change in the trend is observed from N_2 to CO_2 saturation solution as shown in Figure 5.14 to Figure 5.17.

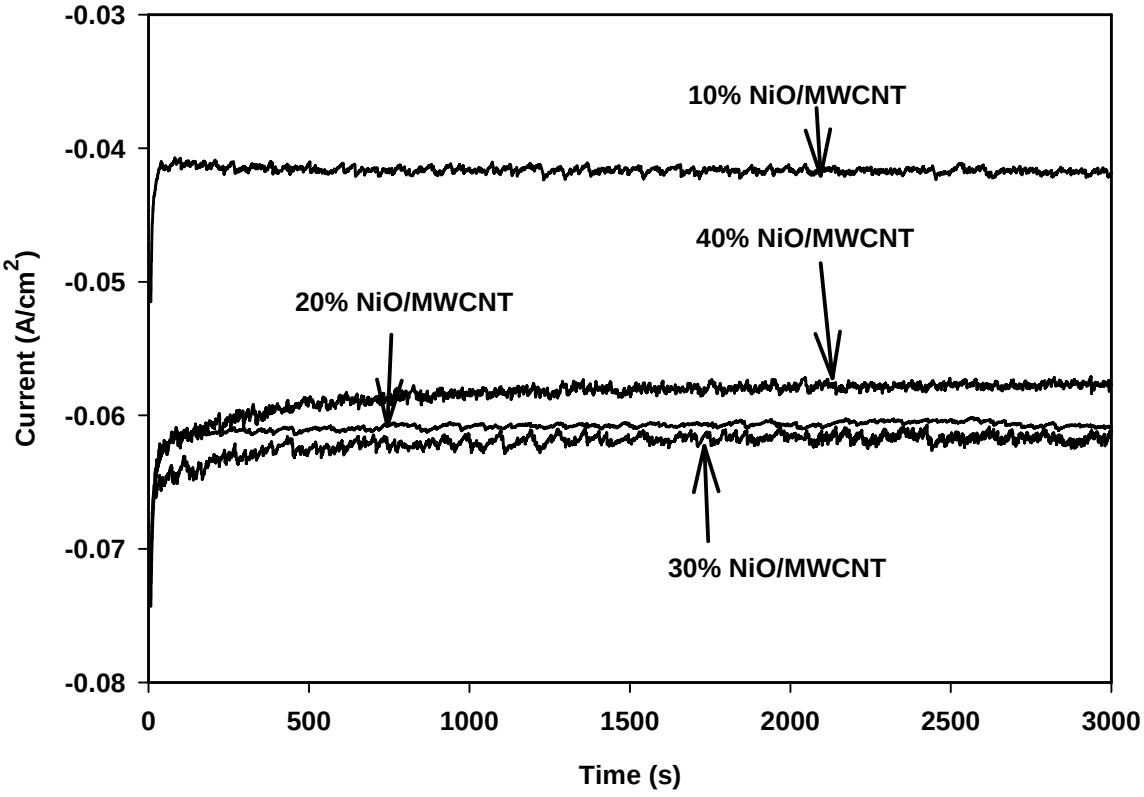

Figure 5.12: CA measurements of different NiO/MWCNT catalysts at -1.7V vs. SCE in 0.5M $NaHCO_3$ solution saturated with CO_2

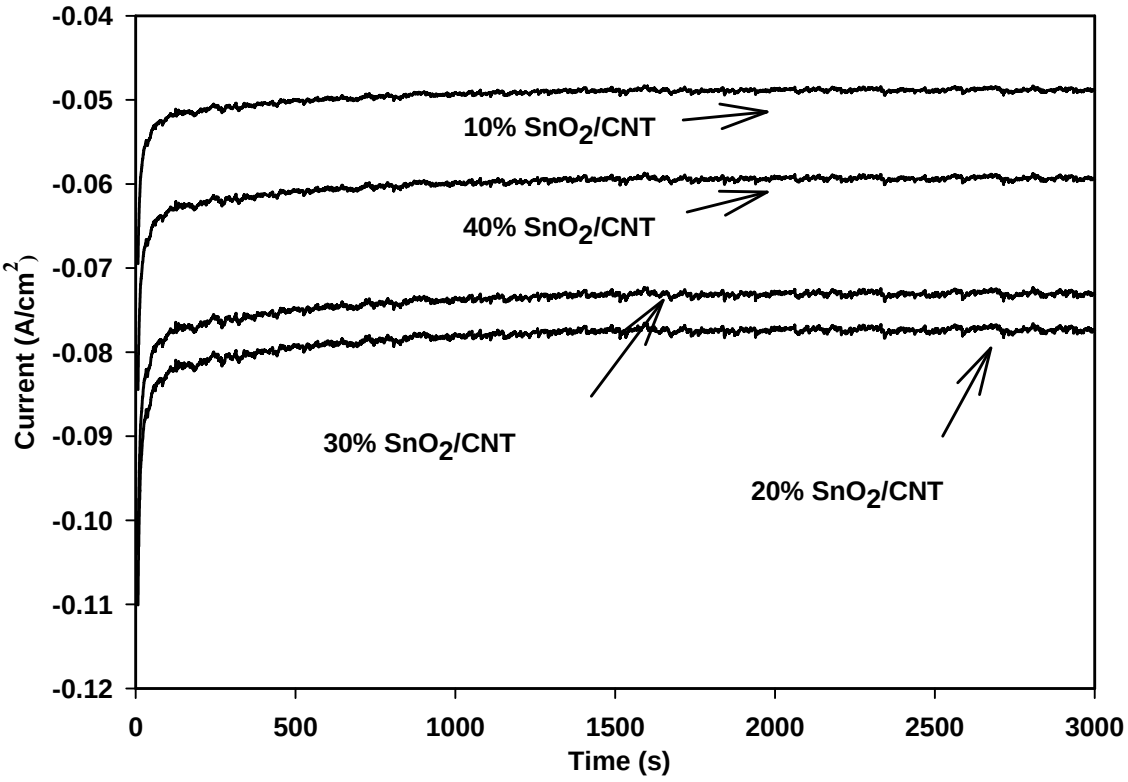

Figure 5.13: CA measurements of different SnO_2/MWCNT catalysts at -1.7V vs. SCE in 0.5M $NaHCO_3$ solution saturated with CO_2

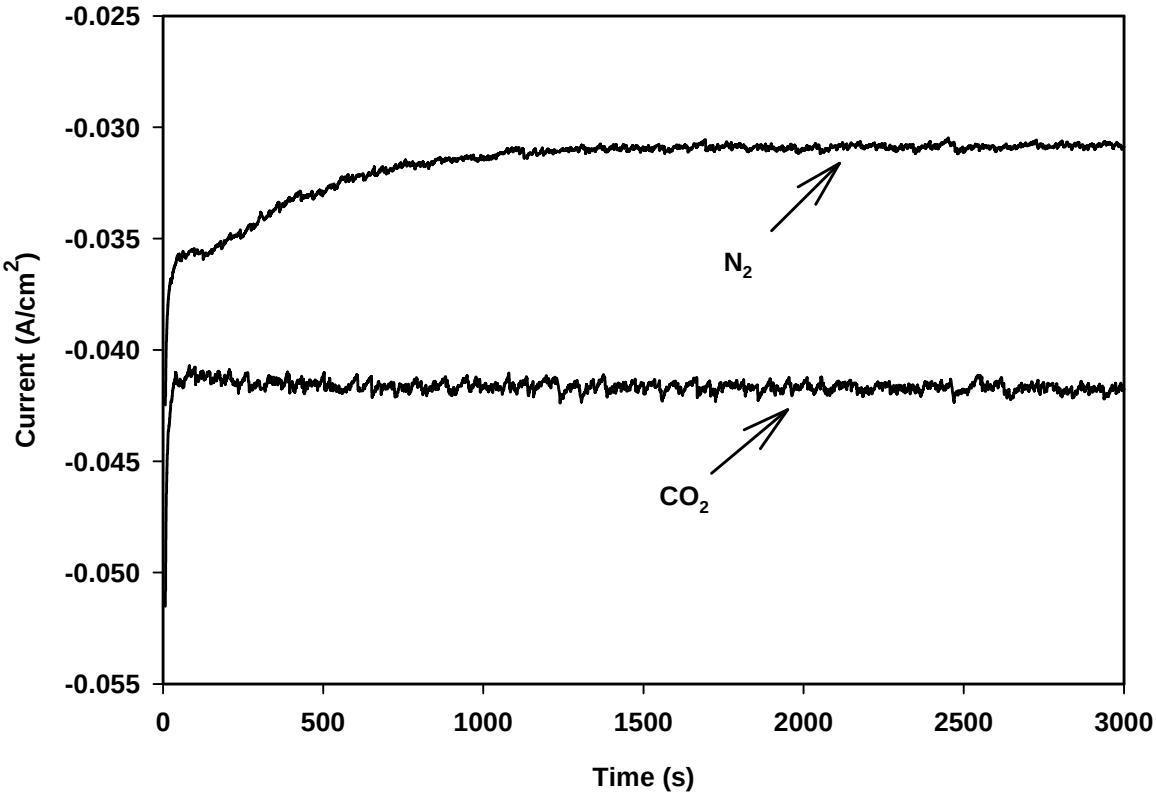

Figure 5.14: CA measurement of 10% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution at -1.7V vs. SCE

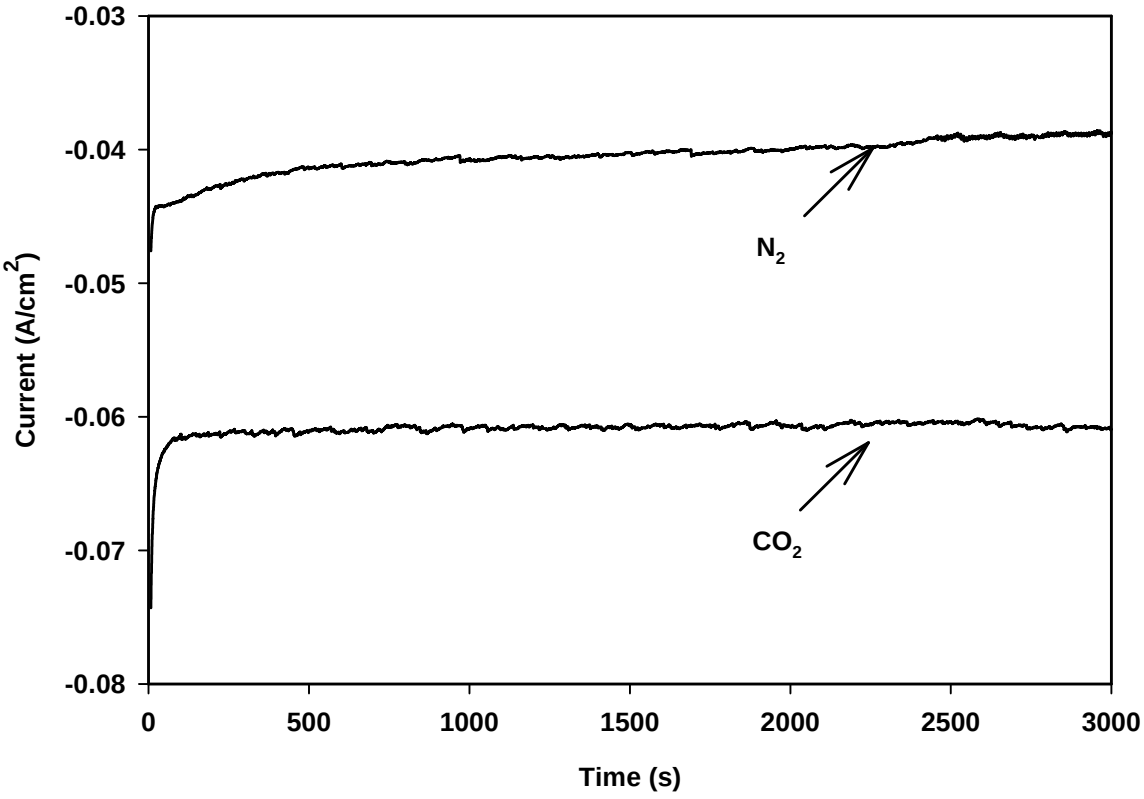

Figure 5.15: CA measurements of 20% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution at -1.7V vs. SCE

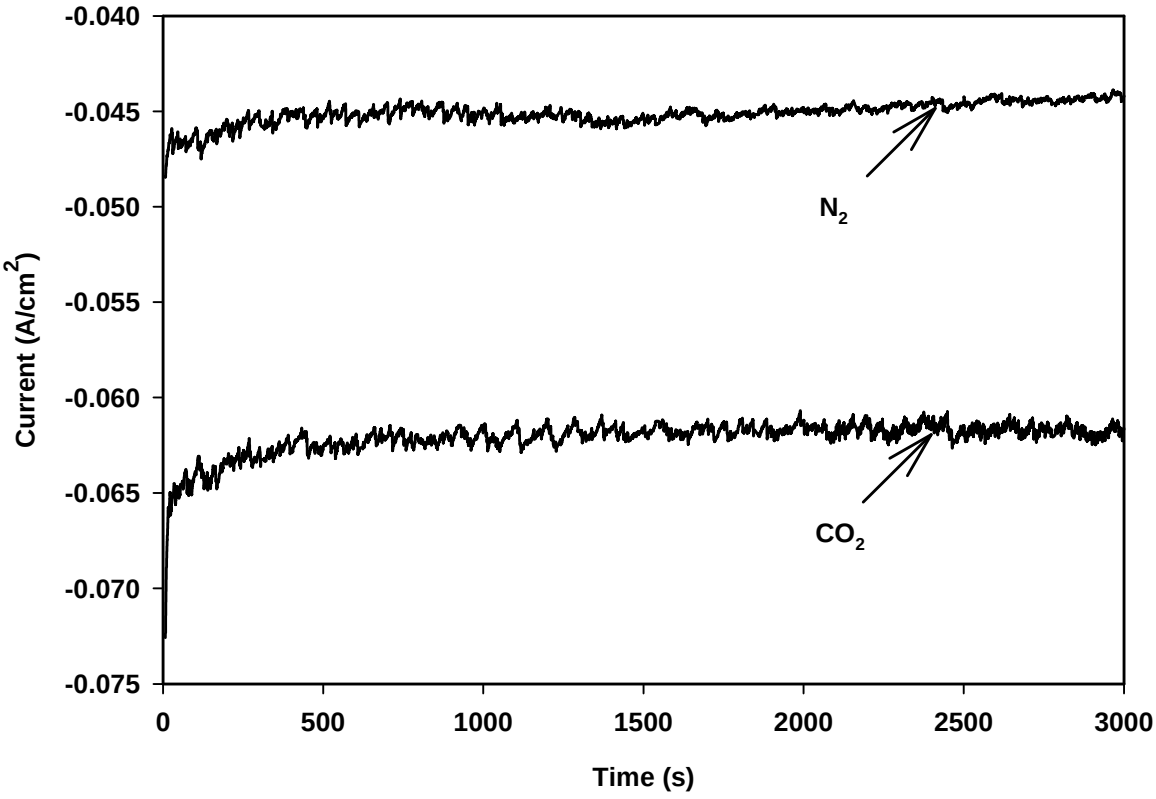

Figure 5.16: CA measurements of 30% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution at -1.7V vs. SCE

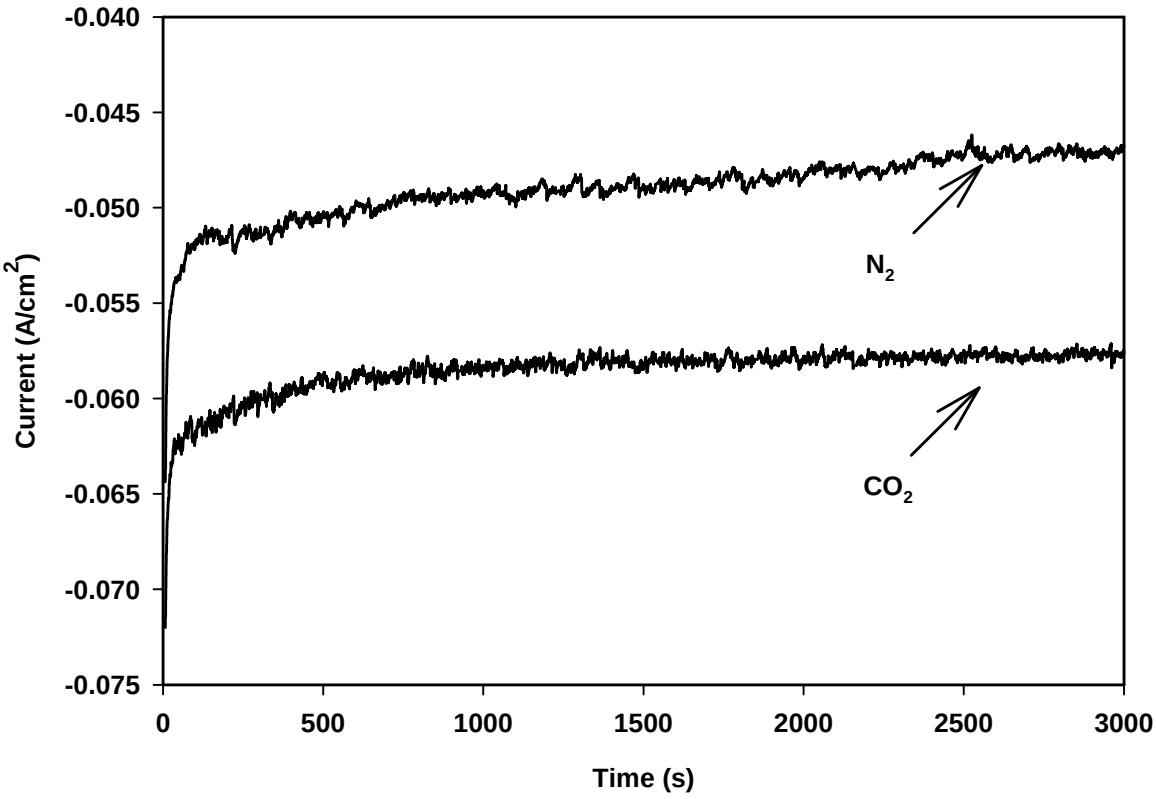

Figure 5.17: CA measurements of 40% NiO/MWCNT catalyst in N_2 and CO_2 saturated 0.5M $NaHCO_3$ solution at -1.7V vs. SCE

Based on the preliminary results from the half cell reaction setup, the 20 % NiO/MWCNT catalyst was further evaluated in the electrochemical reactor. 20 % SnO_2/MWCNT catalyst was not evaluated further due to the limitation in collecting liquid product because liquid product i.e. formate was expected with SnO_2 catalyst. The LSV and CA measurements for 20 % NiO/MWCNT catalyst were also performed and the faradaic efficiencies were also calculated. The faradaic efficiency is defined as the portion of the current passing through the cell that goes to the desired product or the charge used for producing the specific product divided by the charge passed through the cell during the experiment.

At the end of the experiment the product gas samples were collected and analyzed by using a gas chromatography equipped with a TCD detector. When the reaction was carried out with membrane electrode assembly i.e. only the cathode and anode catalyst pressed with membrane only H_2 was the product. This observation is consistent with the results reported by Delacourt et al. as well (Delacourt et al. 2008). By inserting the fiber glass saturated with sodium bicarbonate solution between the membrane and the cathode catalyst, in addition to H_2 gas CO gas was also obtained, this is very useful product as CO and H_2 is collectively known as synThesis gas or syngas.

Figure 5.19 shows the faradaic efficiency for the product obtained at different voltages for 20 % NiO/MWCNT catalyst. The reactions have been performed at four different voltages to see the effect of voltage. Voltage was observed vs. Normal Hydrogen Electrode (NHE).

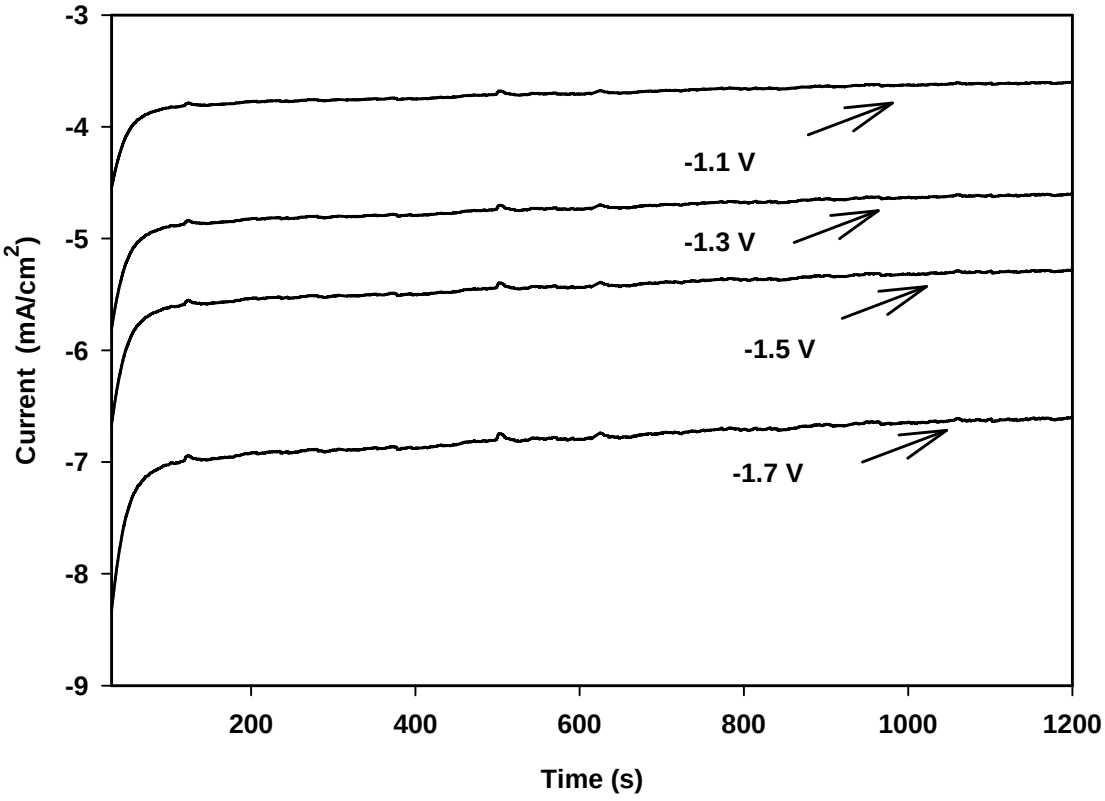

Figure 5.18: CA of 20 % NiO/MWCNT at different voltages vs. NHE

The faradaic efficiency for CO increased slightly from -1.1 V to -1.3 V, but on increasing further towards more negative voltage the efficiency increases further for CO and recorded highest on -1.7 V vs. NHE. The potential of -1.7 V vs. NHE correspond to -1.944 V vs. SCE. The faradaic efficiency for H_2 also increases with increasing the applied voltage. Hydrogen evolution reaction competes with carbon dioxide reduction during electrochemical reaction. Although the hydrogen evolution reaction is not desirable during the course of reaction but the good combination of H_2 and CO (SynThesis Gas) is also a useful product and can be used in the petrochemical industry as an intermediate as well. The evolution of H_2 from the electrochemical carbon dioxide reduction on Ni electrode is evident from the literature. We are getting CO in addition to the H_2. The reduction of carbon dioxide to CO is also reported under elevated pressure on Ni electrode. If we polarize the reaction with more negative potential we might get more products but the main motive of this study to get product at low potential as possible. The faradaic efficiency of CO is 4.52 % at a potential of -1.7 V vs. NHE while H_2 current efficiency is 30.1 % at an active metal oxide loading of 2 mg/cm^2. Yamamoto et al. (2000) reported the current efficiency of around 78 % for CO with a metal loading of 14 mg/cm^2 of Ni/ACF while H_2 current efficiency of about 15 % at -1.9 V vs. SCE . We have increased in efficiency on increasing negative potential for CO while the trend for H_2 also increases with the increase in total faradaic efficiencies as well. The total faradaic efficiency obtained is 35.2 % which is quite low. The faradaic efficiency of up to 100 % is reported in the open literature but mostly in the liquid phase electrolyte and Half Cell reaction setup. The reason of getting such low current efficiency might be due

to high ohmic losses, very low conversion of CO_2 to other products as evident from GC analysis results, failure in collecting the liquid products that might be producing at these voltages due to the limitation in our reactor setup system and of course due to the leakage in collecting the gaseous product.

The reduction of carbon dioxide in the presence of Ni electrode encounter with problem of adsorbing CO strongly on the electrode surface which happens to produce during the reaction preventing further reduction to hydrocarbons. As a result the hydrogen ion produced from the water takes electron and produced hydrogen gas and this is the reason why hydrogen efficiency is increasing at higher voltages. Hydrogen is mostly reported to be a major product during the reduction of carbon dioxide at the nickel electrode but with increasing pressure which we are assume to be getting with these nanotubes strongly suppress hydrogen production and at the same time forcing adsorb CO to be evolved i.e. desorb CO in the gas phase and this phenomena is more prominent at more negative voltage. As a result CO is also producing along with the hydrogen. This mechanism is also proposed by Kudo et.al (1993).

Carbon monoxide and hydrogen is collectively known as synthetic gas or syngas. The product is very useful if it in the proper ratio. Along with the faradaic efficiencies we have also calculated the CO to H_2 obtained at different voltages with 20 % NiO/MWCNT catalyst as shown in Figure 5.20. Ratio of 1:1 is suitable for methane synThesis while the 1:2 ratio of CO to H_2 is useful for the production of methanol. Although we are not getting gases in these two ratios but our best results lies in the voltage range of -1.3 V vs. NHE which is 0.37726 but the faradaic efficiency is low while the ratio of CO to H_2 at

voltage of -1.7V vs. NHE is 0.1472 with overall efficiency of 35.2 %. Further improvement can be made by varying potential and by adding promoters in the NiO catalyst to get the more useful ratios and further modification is needed to enhance the current efficiency.

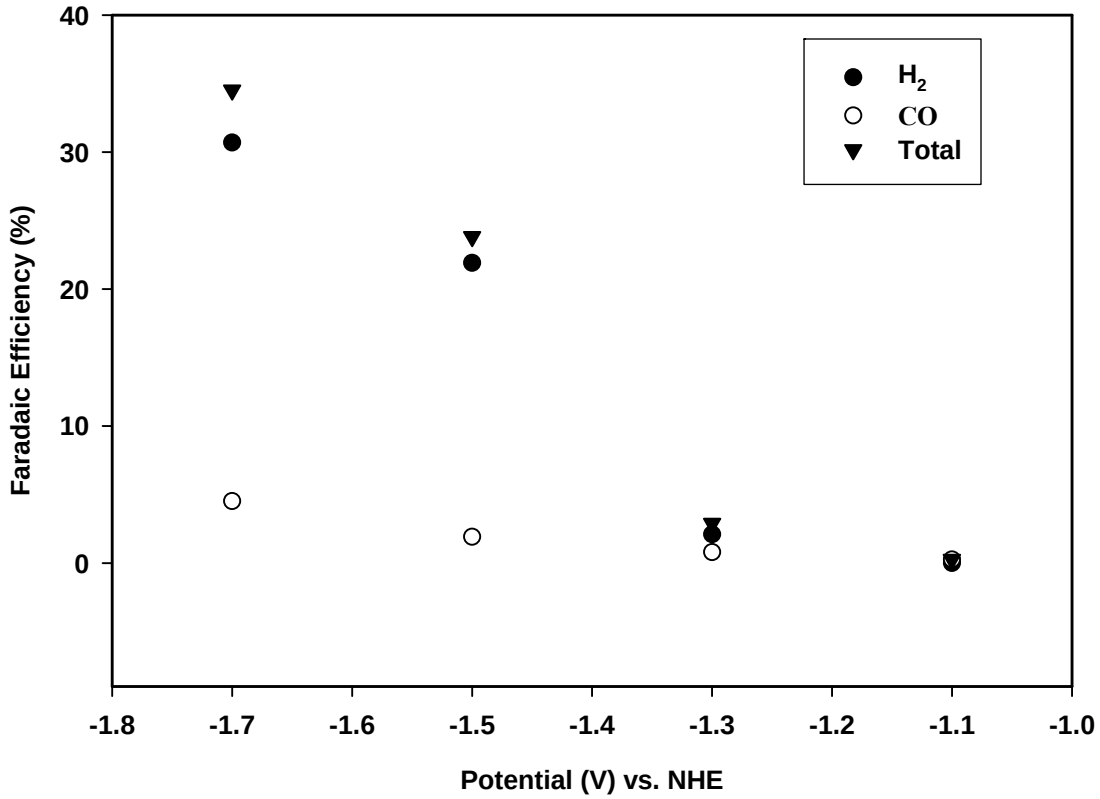

Figure 5.19: Faradaic Efficiency for 20 % NiO/MWCNT catalyst

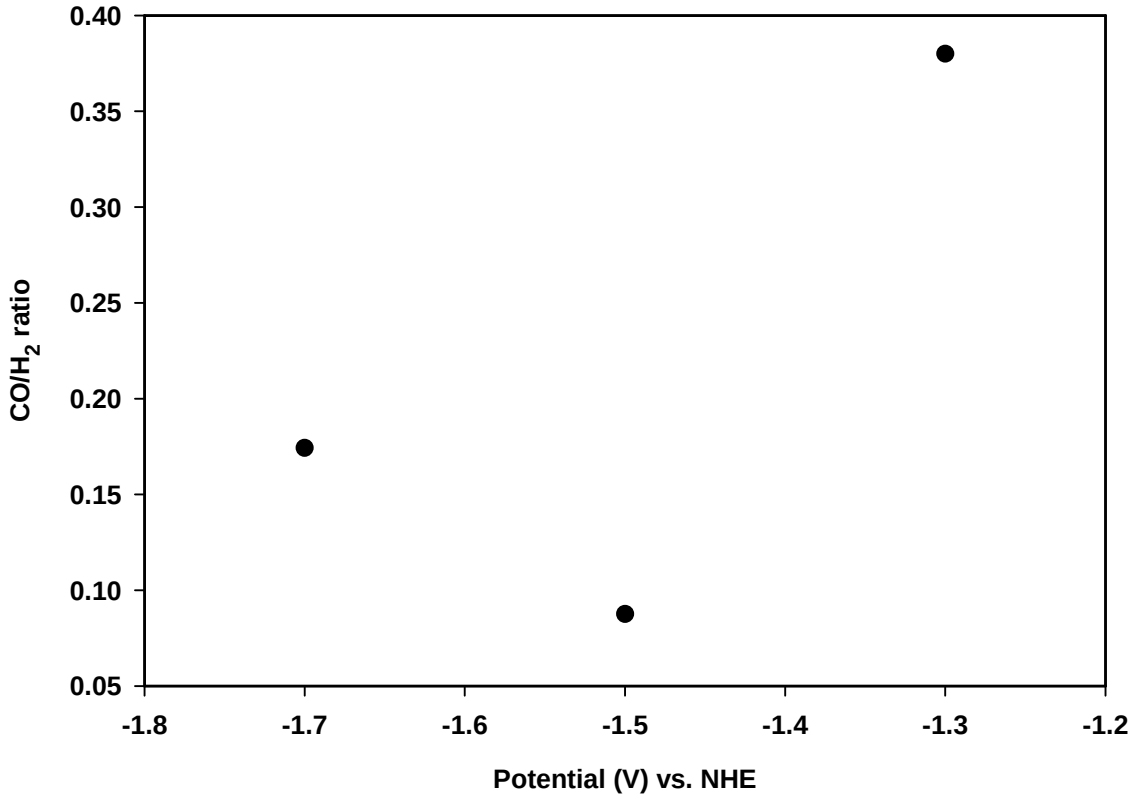

Figure 5.20: CO/H_2 ratio of 20 % NiO/MWCNT catalyst at different voltages

Chapter 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The following are the conclusion of this study:

1. The percentage loading by weight of 20 % NiO and SnO_2 on MWCNT was found to be the best among the catalyst samples prepared of 10 %, 20 %, 30 % and 40 % using dry impregnation method.
2. The size of the NiO and SnO_2 crystallites was increased with increasing metal oxide content. Dispersion of the NiO content decreases at higher loading of 40 % and the particle size also starts agglomerating at this higher loading as revealed by scanning electron microscopy (SEM). Actual quantity of the elements differ from the nominated ones with a difference of 5.123 % and 6.04 % in case of 20 % and 40 % NiO loading respectively with the help of the EDX assembly associated with SEM equipment.
3. Among the two phases NiO (111) and NiO (200), the intensity of NiO (200) was highest and the crystalline size was calculated by taking the XRD data of this phase with the help of Scherrer's equation.
4. 20 % NiO/MWCNT catalyst produces the highest current among the given sample evaluated in the half cell and electrochemical reactor (reverse fuel cell) set up. Half cell reaction studies were performed to screen out the best catalyst

among the given samples prepared by taking into account the amount of current product by each catalyst. .

5. The total faradaic efficiency of 35.2 % was obtained at the potential of -1.7 V vs. NHE with 20 % NiO/MWCNT catalyst evaluated in electrochemical reactor. The use of MWCNT's seems to produce the nano scale effect which helps in producing high pressure effect at ambient condition. The production of CO along with H_2 showed good sign of utilizing this catalyst for efficient carbon dioxide reduction to useful intermediate products like Synthetic Gas.

6.2 Recommendations

Based on the study performed the following recommendations will be useful to carry this work further

1. For better dispersion and to get maximum loading of the active component in the catalyst, other techniques such as Precipitation Deposition method or Sol Gel Method should be employed to get the maximum benefit from the same system.
2. Characterization techniques such as BET surface area and adsorption /desorption studies should be carried out to get more insight in the catalyst pore and the surface. Transmission electron microscopy (TEM) might be a useful for visualizing the closest structure of the catalyst particle and atomic absorption spectroscopy (AAS) or inductively coupled plasma spectroscopy (ICPS) can be performed to determine the actual metal oxide content in the catalyst samples.

3. Half cell setup was used to carry out the screening of the catalyst based on the amount of the current produced. The cell should be modified to be leak proof. By doing so the amount of product produced can be measured that might be useful for better comparison to the faradaic efficiencies obtained from the Electrochemical Reactor as well.
4. Electrochemical reduction carbon dioxide is highly favorable in alkaline medium. So there is a great need in developing solid electrolyte membrane which is alkaline in nature to make the electrochemical reactor based on reverse fuel cell setup more successful.

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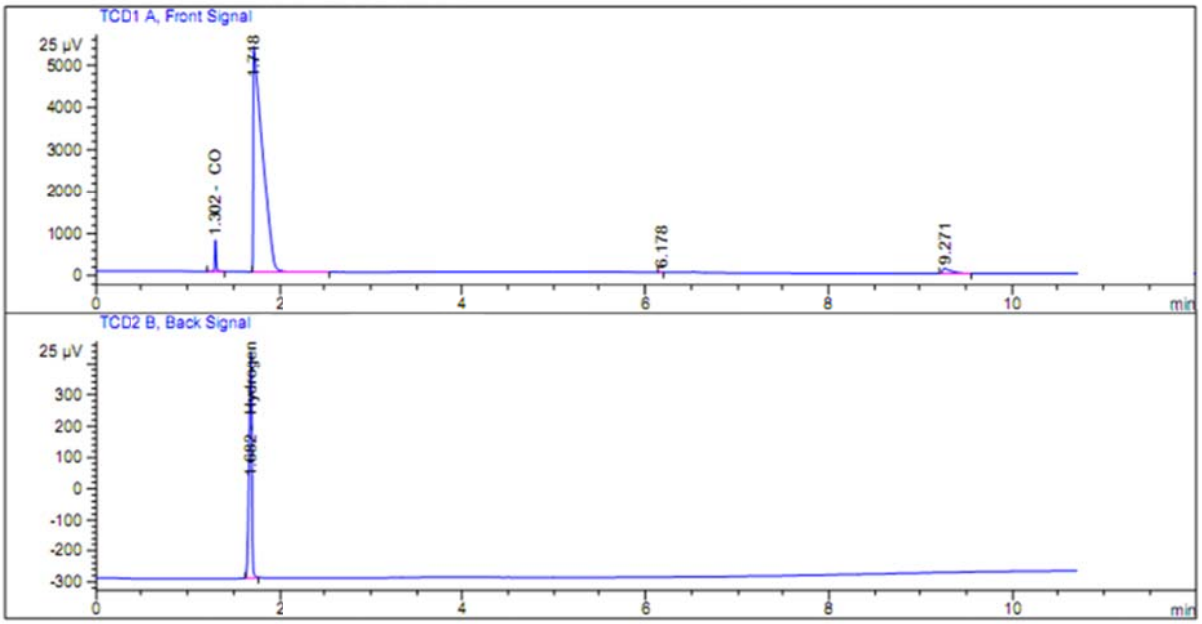
APPENDIX A: GAS CHROMATOGRAPH

GAS CHROMATOGRAPH (GC) OF 20 % NiO/MWCNT CATALYST EVALUATED IN AN ELECTROCHEMICAL REACTOR AT A POTENTIAL OF -1.7 V VS. NHE

```
Acq. Operator    : Shahid
Acq. Instrument : Instrument 1                    Location :    -
Injection Date  : 10/11/2011 11:12:49 PM
                                                 Inj Volume : Manually
Acq. Method     : C:\CHEM32\1\METHODS\RGA-GASPPM.M
Last changed    : 10/11/2011 11:03:27 PM by Shahid
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\RGA-GASPPM.M
Last changed    : 1/15/2012 9:31:48 PM by Shahid
                  (modified after loading)
Sample Info     :
```




```
                        External Standard Report

Sorted By             :      Signal
Calib. Data Modified  :      4/24/2011 12:36:36 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD1 A, Front Signal

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]         [25 µV*s]                [ppm]
-------|------|----------|----------|----------|--|------------------
  1.302 BB      802.90570    3.46790 2784.39347    CO
  1.418           -          -          -         Methane
  2.703           -          -          -         Ethylene
  7.981           -          -          -         Methanol

Totals :                              2784.39347
```

Signal 2: TCD2 B, Back Signal

RetTime [min]	Type	Area [25 µV*s]	Amt/Area	Amount [ppm]	Grp	Name
1.682	BB	1487.92004	11.75840	1.74956e4		Hydrogen

Totals : 1.74956e4

2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found

*** End of Report ***

Method C:\CHEM32\1\METHODS\RGA-GASPPM.M

Calibration Table

Calib. Data Modified : 4/24/2011 12:36:36 PM

Rel. Reference Window : 5.000 %
Abs. Reference Window : 0.500 min
Rel. Non-ref. Window : 5.000 %
Abs. Non-ref. Window : 0.500 min
Uncalibrated Peaks : not reported
Partial Calibration : Yes, identified peaks are recalibrated
Correct All Ret. Times: Yes, even for non-identified peaks

Curve Type : Linear
Origin : Included
Weight : Equal

Recalibration Settings:
Average Response : Average all calibrations
Average Retention Time: Floating Average New 75%

Calibration Report Options :
Printout of recalibrations within a sequence:
Calibration Table after Recalibration
Normal Report after Recalibration
If the sequence is done with bracketing:
Results of first cycle (ending previous bracket)

Signal 1: TCD1 A, Front Signal
Signal 2: TCD2 B, Back Signal

RetTime [min]	Sig	Lvl	Amount [ppm]	Area	Amt/Area	Ref	Grp	Name
1.274	1	1	9.39070e4	2.70790e4	3.46790			CO
1.418	1	1	997.00000	20.91007	47.68037			Methane
1.671	2	1	1103.00000	93.80526	11.75840			Hydrogen
2.703	1	1	981.00000	31.34278	31.29907			Ethylene
7.981	1	1	504.00000	15.43889	32.64482			Methanol

1 Warnings or Errors :

Warning : Overlapping peak time windows at 1.274 min, signal 1

Peak Sum Table

No Entries in table

APPENDIX B: FARADAIC EFFICIENCY CALCULATION

FARADAIC EFFICIENCY CALCULATION OF 20 % NiO/MWCNT CATALYST EVALUATED IN AN ELECTROCHEMICAL REACTOR AT VARIOUS POTENTIALS vs. NHE

Voltage		ppm(v)	ppm	Density	Density	mass	molar	molar flow	molar fraction	I	T	R	P		F	Fv	Fv	Fm	I (A)	FE	Total FE	CO/H_2
V /NHE		ml/ml	m^3/m^3	kg/m^3	g/m^3	g/m^3	mol/m^3	mol/sec		mA	K	J/mol/K	N/m^2	e	C/mol	ml/min	m^3/sec	mol/s	A	%	%	
-1.1	CO	88.4	0.0000884	1.165	1165	0.102986	0.00368	1.22602E-09	8.99805E-05	90	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	9.00E-02	2.63E-01	2.63E-01	*
	H_2	0	0	0.0899	89.9	0	0	0	0	90	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	9.00E-02	0.00E+00		
-1.3	CO	339.9	0.0003399	1.165	1165	0.395984	0.01414	4.71409E-09	0.000345977	115	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.15E-01	7.91E-01	2.89E+00	0.3773
	H_2	833.95	0.000834	0.0899	89.9	0.074972	0.03749	1.24954E-08	0.00091706	115	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.15E-01	2.10E+00		
-1.5	CO	946	0.000946	1.165	1165	1.10209	0.03936	1.31201E-08	0.000962913	132	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.32E-01	1.92E+00	2.38E+01	0.0877
	H_2	9.99E+03	0.0099893	0.0899	89.9	0.898042	0.44902	1.49674E-07	0.010984865	132	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.32E-01	2.19E+01		
-1.7	CO	2784	0.002784	1.165	1165	3.24336	0.11583	3.86114E-08	0.002833775	165	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.65E-01	4.52E+00	3.52E+01	0.1473
	H_2	1.75E+04	1.75E-02	0.0899	89.9	1.572854	0.78643	2.62142E-07	0.019239189	165	298.15	8.314	101325	2	96487	20	3.33E-07	1.36254E-05	1.65E-01	3.07E+01		

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